Edinburgh, UK
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SWISS NATIONAL SCIENCE FOUNDATION

Stockholm University

Structure determination of polycrystalline materials using X-rays and electrons

Stef Smeets

Stockholm University

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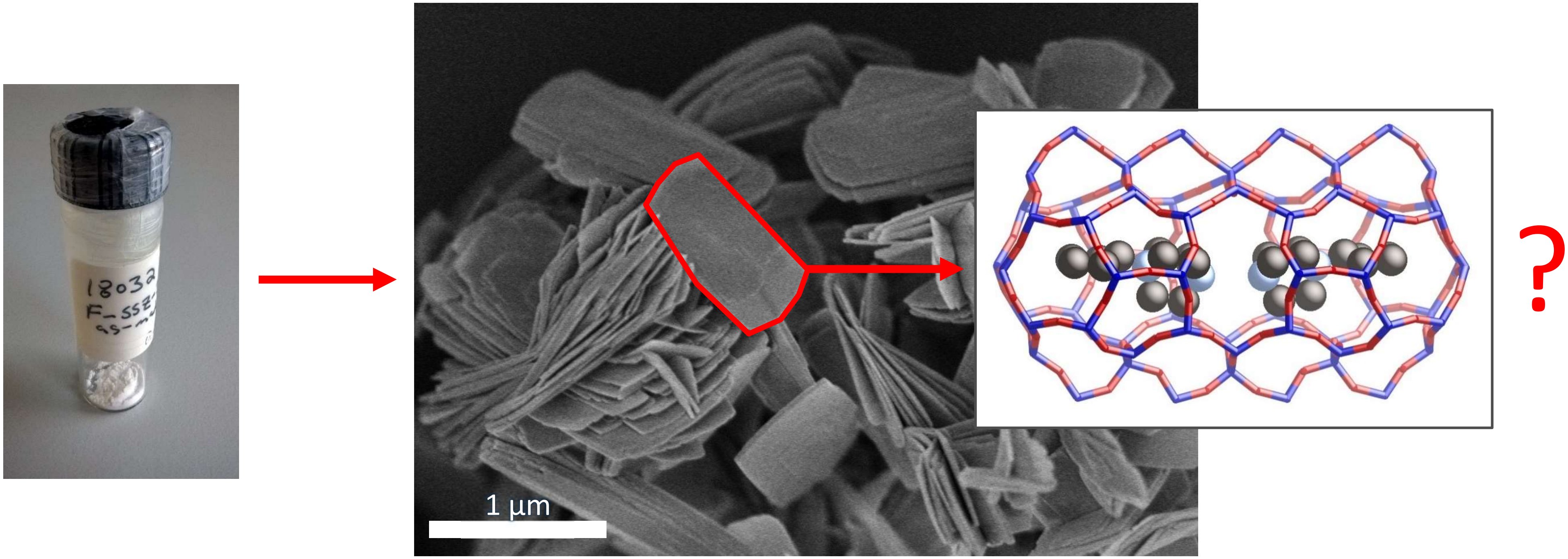
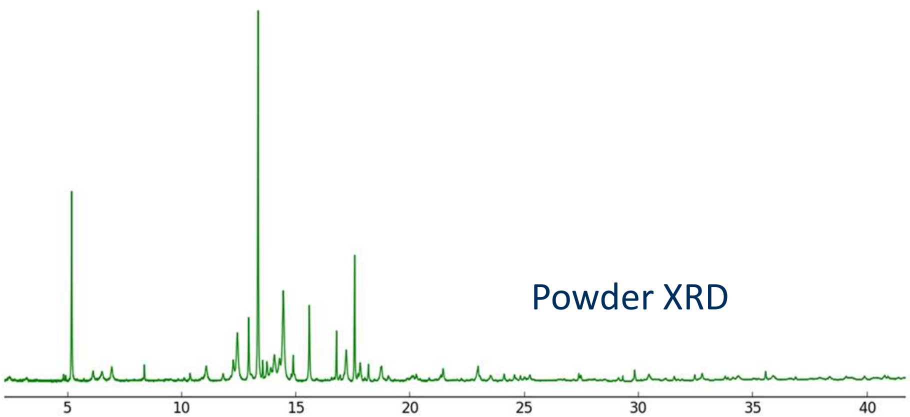
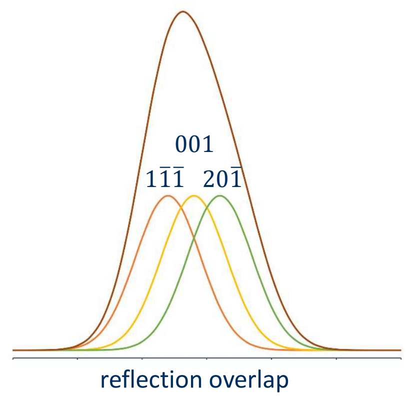
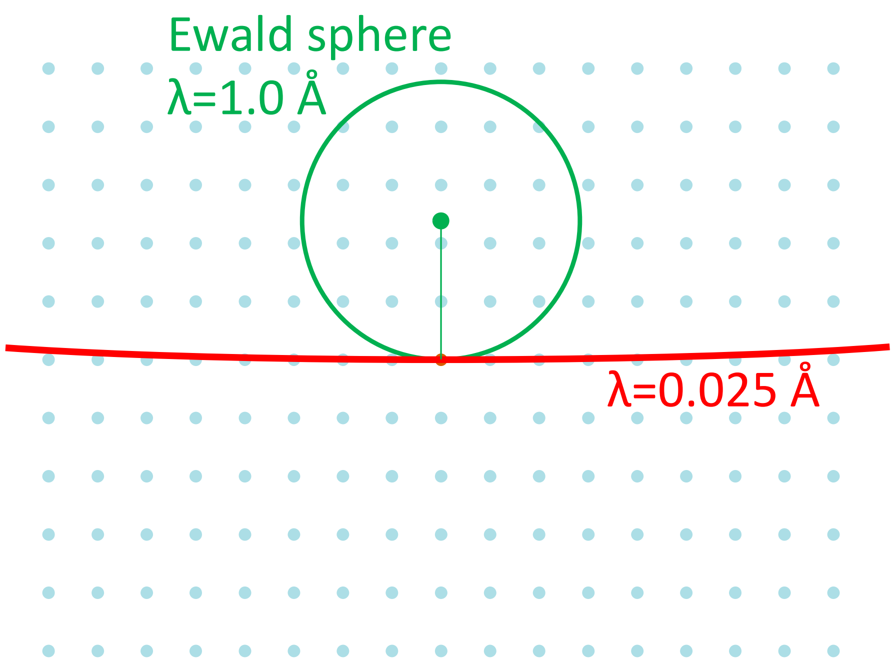

1 µm
?


5
10
15
20
25
30
35
40

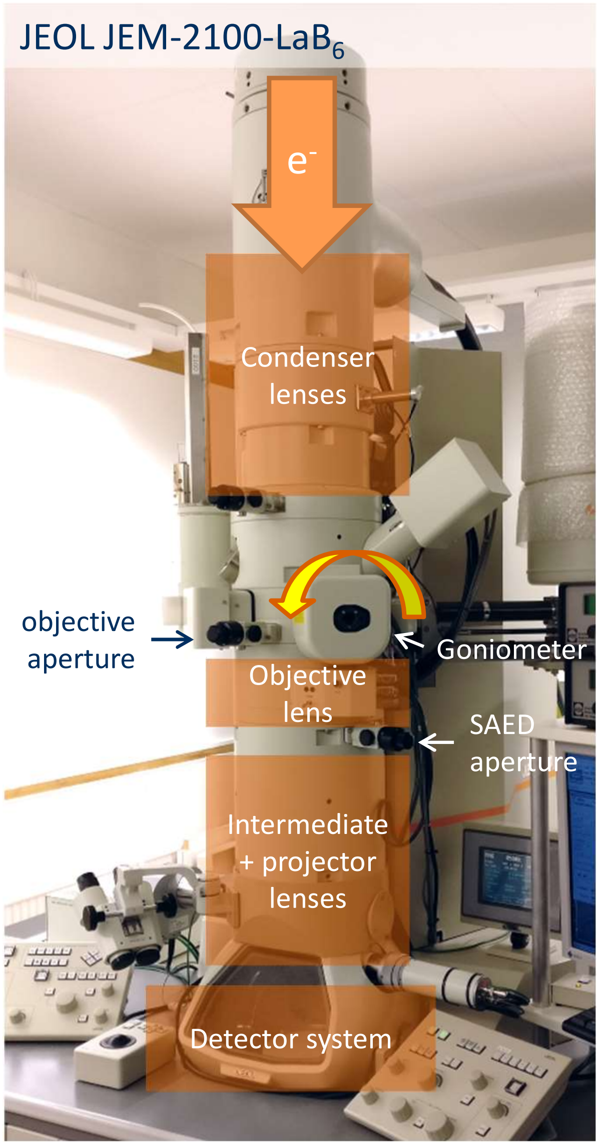
Powder XRD


001
1$\bar{1}\bar{1}$
20$\bar{1}$
reflection overlap

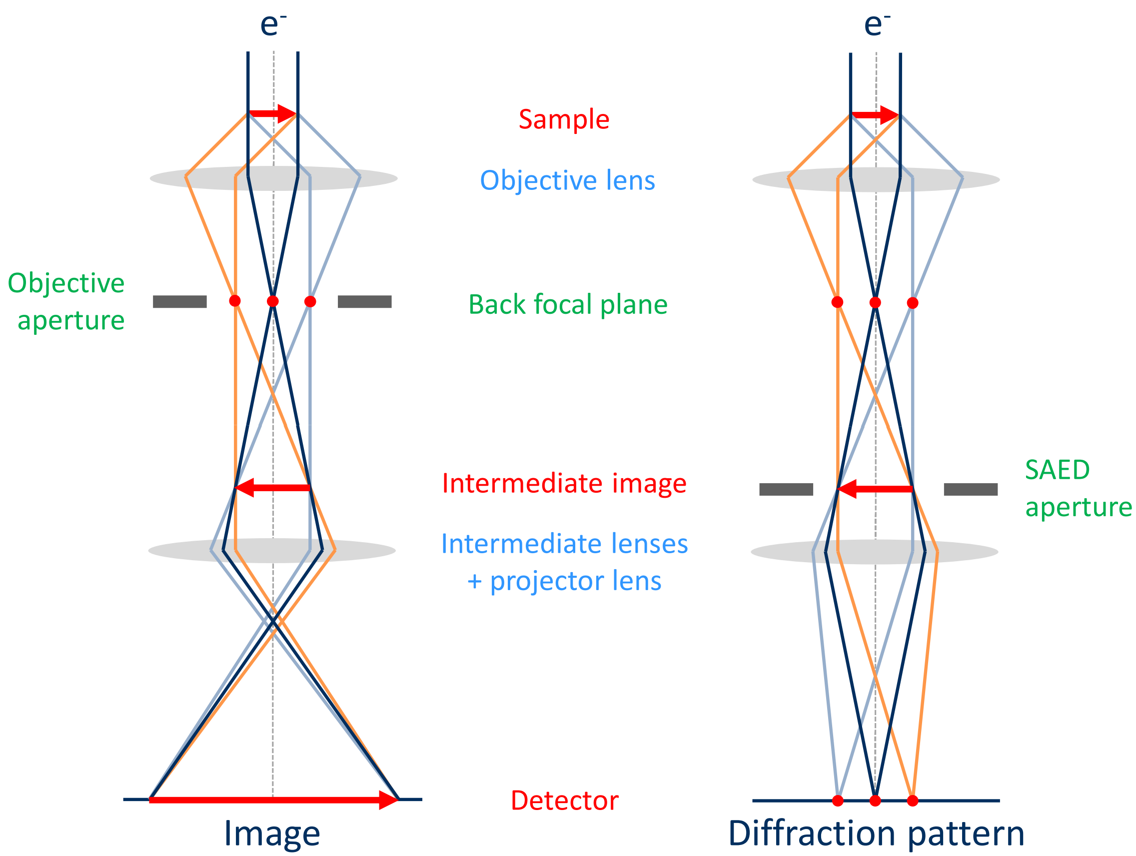
Electrons as a radiation source



- Accelerating voltage: 100 to 300 keV
- Wavelength: 0.0251 Å @ 200 keV
- Probe electrostatic potential
- Strong interaction (10^6 stronger than X-rays)
- Require small samples (< 1 μm)
- High vacuum (<10^{-3} mbar)



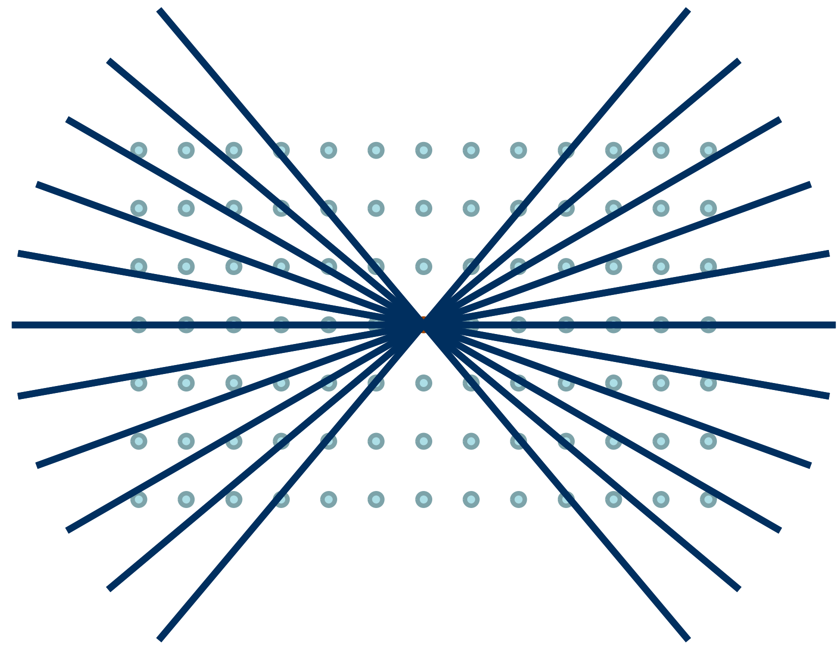
Electron ‘diffractometer’



Single crystal electron diffraction

Limitations

- Dynamical (multiple) scattering
- Beam damage
- Missing wedge
- Goniometer mechanics



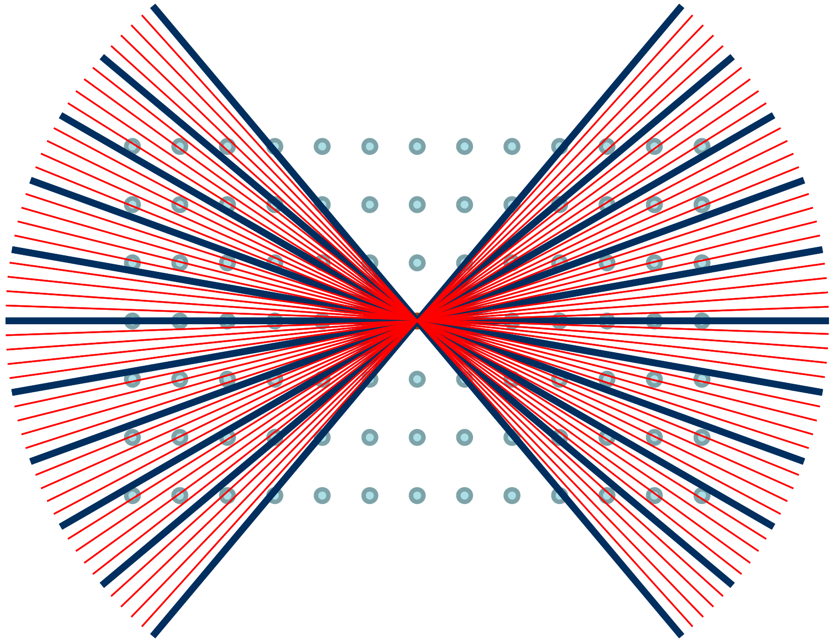
- Filling the gaps:
  - Beam tilt (RED)
  - Precession (ADT, pEDT)
  - Continuous rotation
    (fast EDT, microED, IEDT, CRED)

- More than 200 structures solved (Yun *et al.*, IUCrJ (2015), 2:267)

Fine slicing using beam tilt (RED)

Zhang *et al.*, Z. Krist. (2010), 225:94

Wan *et al.*, J. Appl. Cryst. (2013), 46:1863



Tilt range: up to 150°

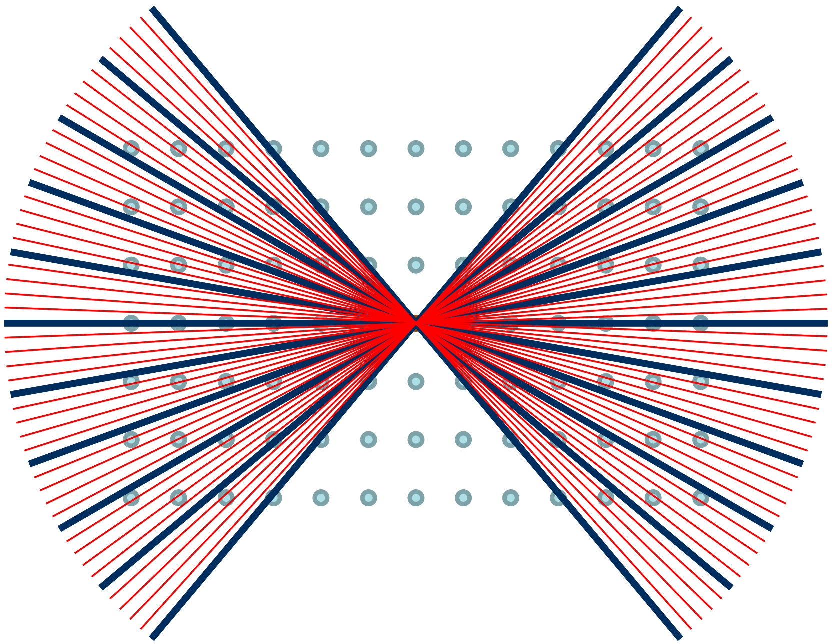
Goniometer tilt: ~2.0°

Beam tilt: ~0.1°

30-60 minutes

Fine slicing using beam tilt (RED)

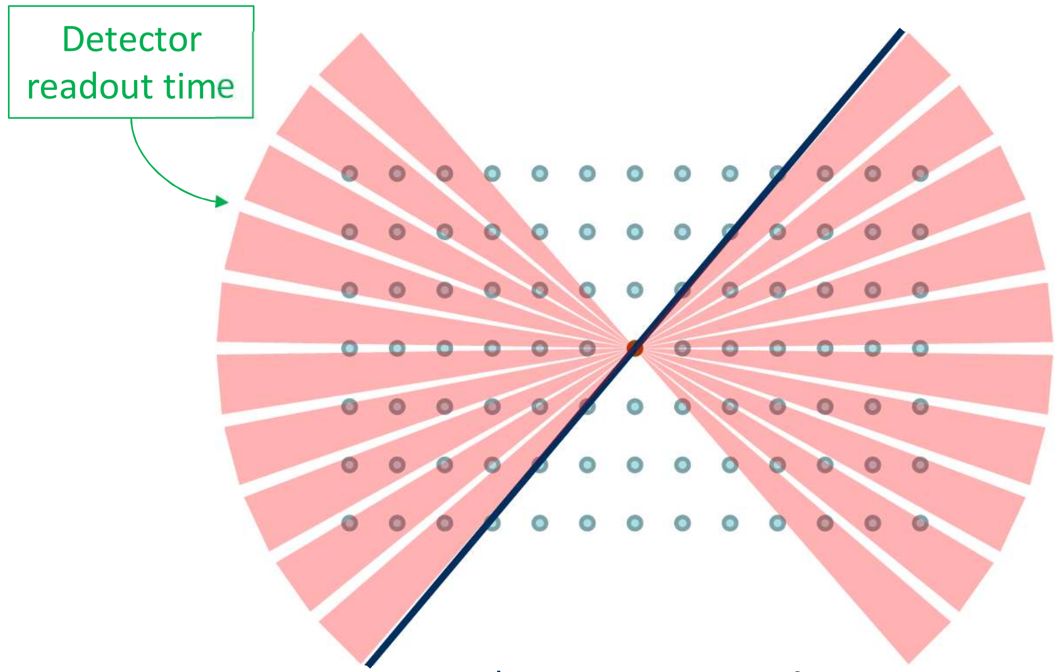
Zhang *et al.*, Z. Krist. (2010), 225:94
Wan *et al.*, J. Appl. Cryst. (2013), 46:1863



Tilt range: up to 150°
Goniometer tilt: ~2.0°
Beam tilt: ~0.1°
30-60 minutes

Continuous rotation method (CRED)

Nederlof *et al.*, Acta Cryst. D (2013), 69:1223
Nannenga *et al.*, Nat. Methods (2014), 11:927
Gemmi *et al.*, J. Appl. Cryst. (2015), 48:718
Wang *et al.*, Chem. Commun., (2017), 53:7018

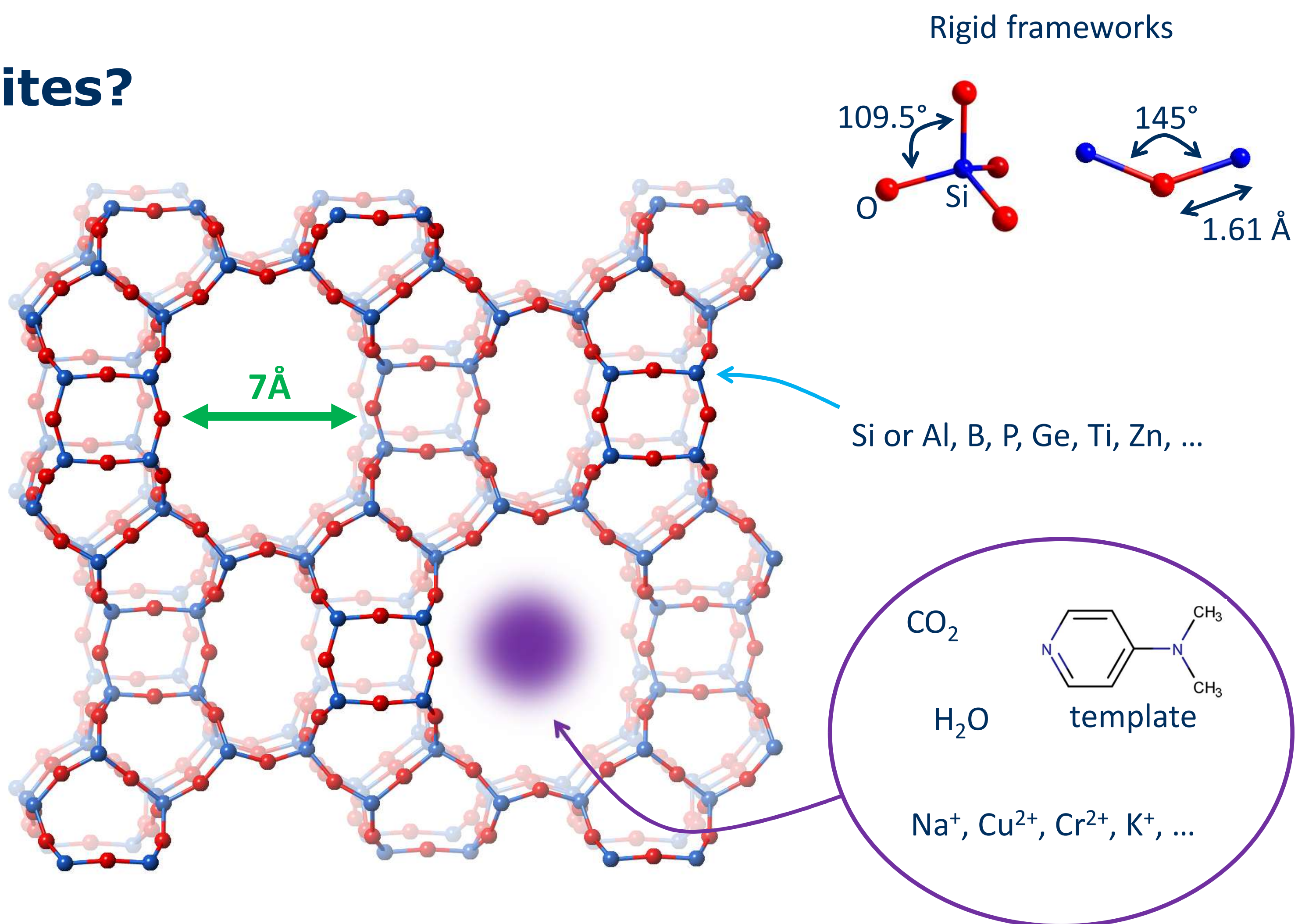


Tilt range: up to 150°
Oscillation angle: 0.1-0.5°
Rotation speed: 0.5-2.0°/s
1-5 minutes

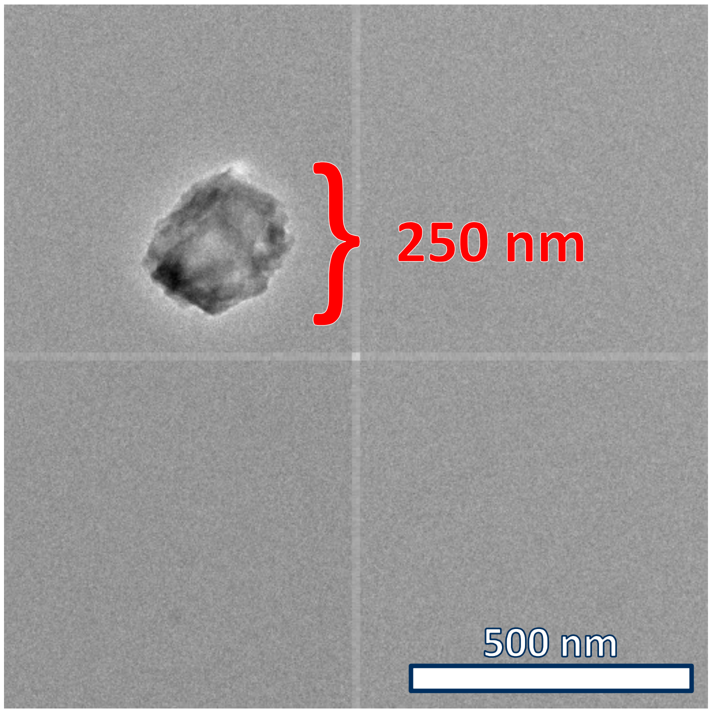
What are zeolites?

Microporous
Aluminosilicates

Catalysis
Dessicants
Molecular sieves
Gas separation
Gas traps
Detergents
Cracking processes
Nuclear waste treatment
Pet litter
Soil additive
DeNOx
...



Example: Mordenite



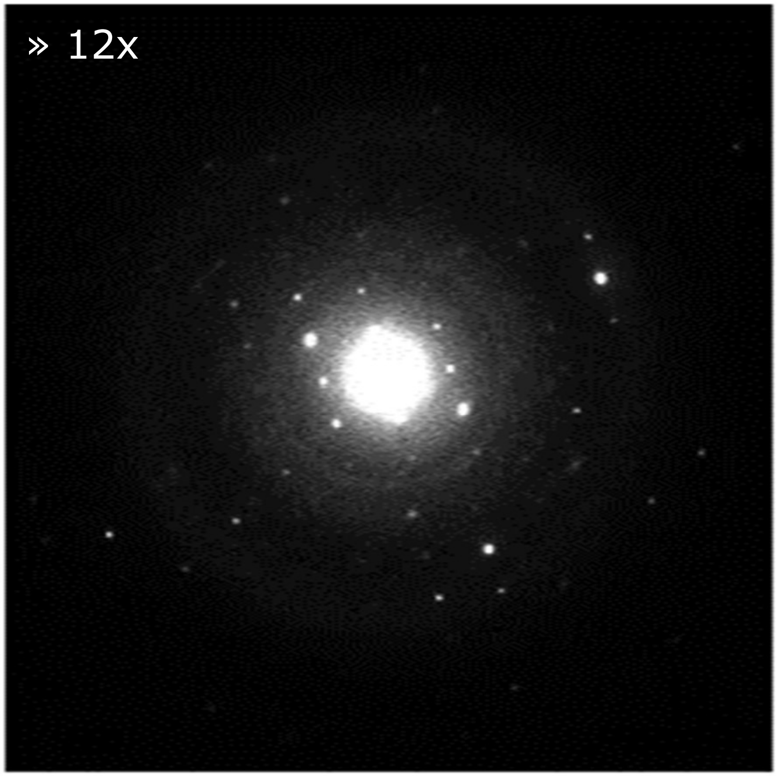
Zeolite
Porous aluminosilicate

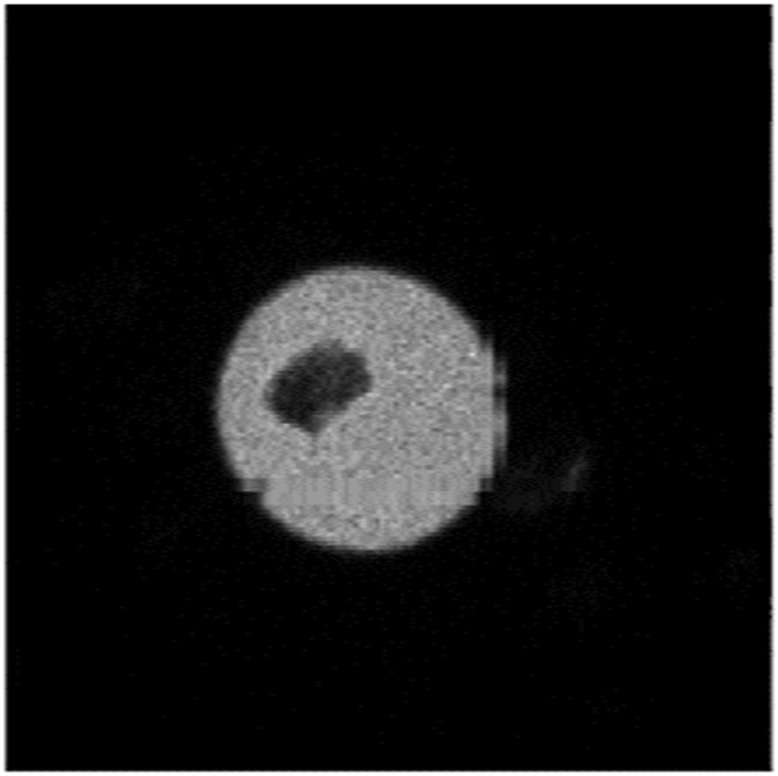
$Si_{48}O_{96}$

Orthorhombic $Cmcm$
a = 18.11 Å
b = 20.53 Å
c = 7.528 Å

Mordenite

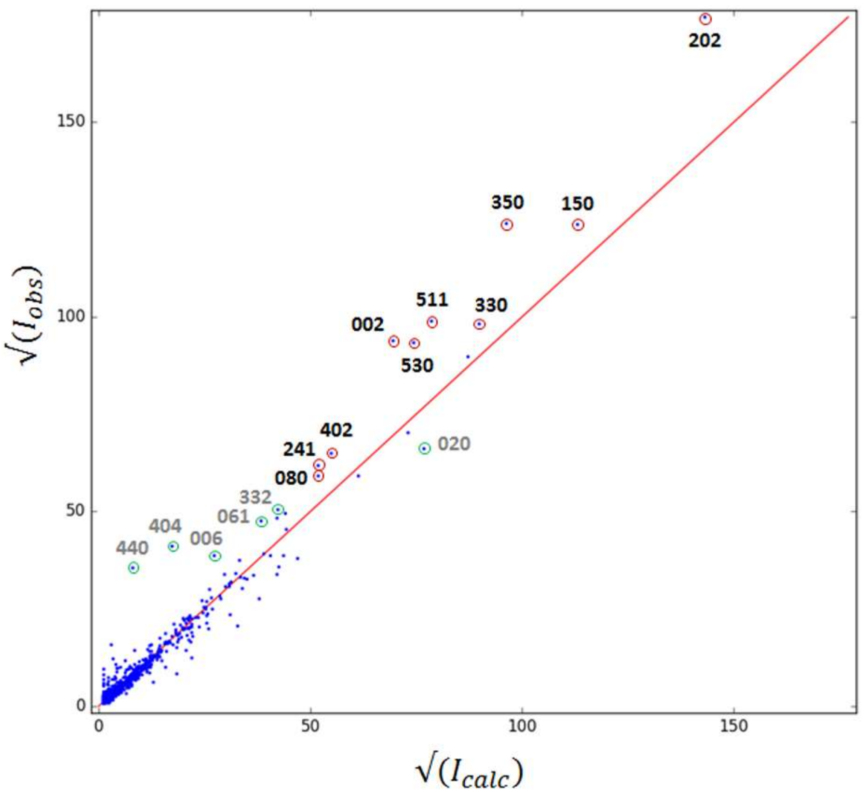
Rotate: -43.90° to 58.65° @ 0.45°/s (102.55°)
Exposure: 0.5 s, oscillation angle: 0.23°





Data collected with M.O. Cichocka (Stockholm University)

Structure refinement



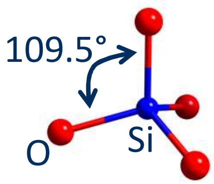
Data reduction	**XDS**
Compl. ($Cmcm$)	93.6 %
I/σ	6.25
Resolution	0.80 Å
R_{meas}	0.108
R_{obs}	0.088
R_{exp}	0.087
Refinement	**ShelXL**
Reflections (unique)	1585
Reflections (F_o>4σ(F_o))	1140
$R1$ (F_o>4σ(F_o))	0.158
$R1$ (all)	0.175
Parameters	96
Restraints	0
GOOF	1.611

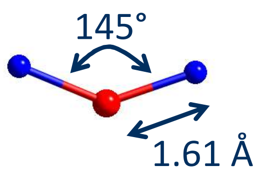
Refinement by M.O. Cichocka (Stockholm University)

Framework structure

Si—O	1.614 ± 0.012 Å
Si—O—Si	109.5 ± 1.9°
O—Si—O	153.3 ± 12.0°

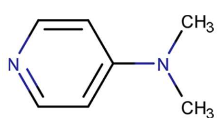
Rigid frameworks





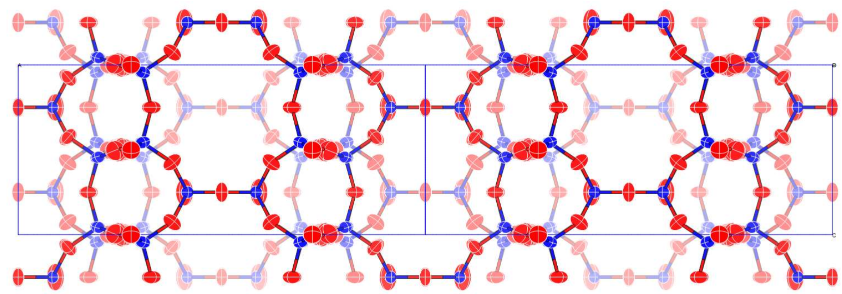
CO_2

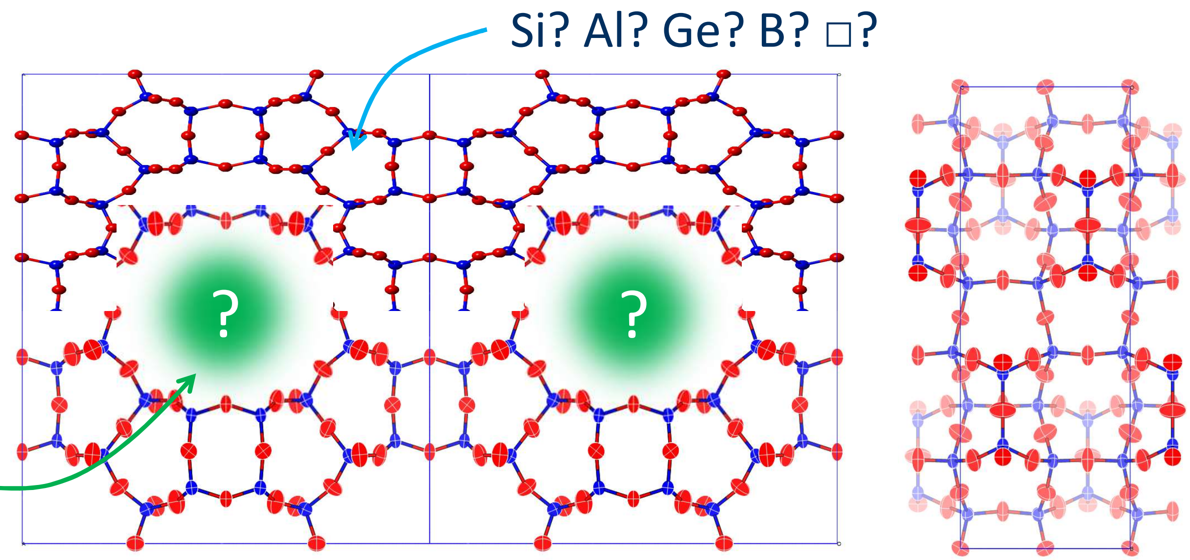
H_2O



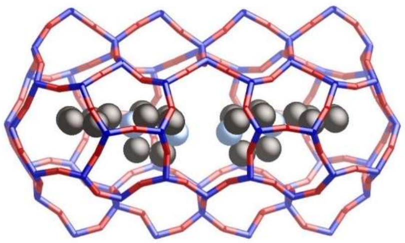
template

Na^+, Cu^{2+}, Cr^{2+}, K^+, …

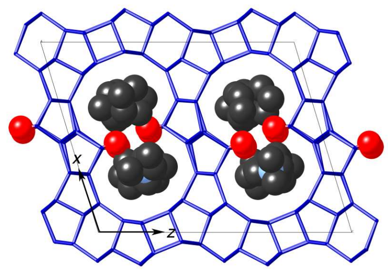




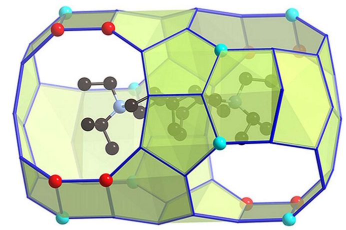
Structure determination using X-rays and electrons



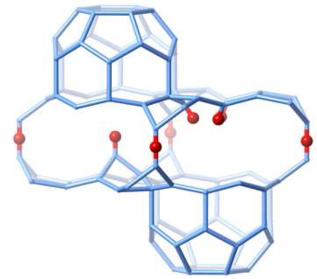
SSZ-45; S. Smeets *et al.*, *Chem. Mater.*, 2014



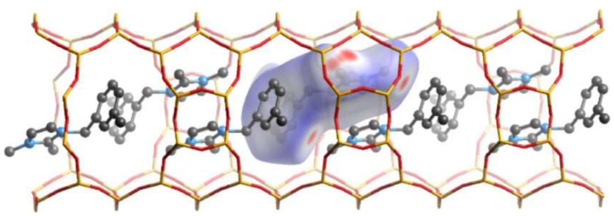
SSZ-61; S. Smeets *et al.*, *Angew. Chem.*, 2014



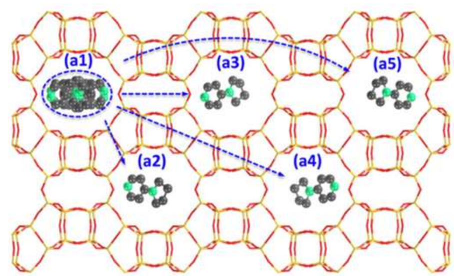
SSZ-87; S. Smeets *et al.*, *J. Am. Chem. Soc.*, 2015



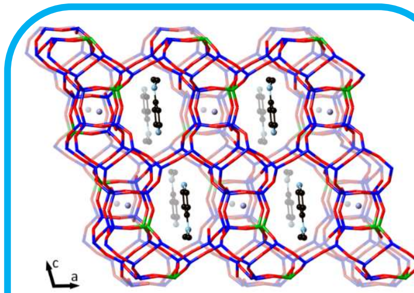
SSZ-70; S. Smeets *et al.*, *J. Am. Chem. Soc.*, 2017



CIT-13; J.H. Kang *et al.*, *Chem. Mater.*, 2017



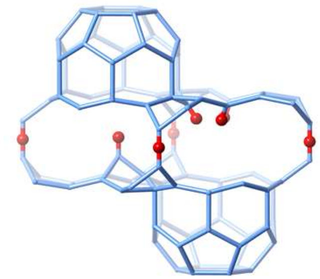
SCM-14; Y. Luo *et al.*, *Chem.-Eur. J.*, 2017



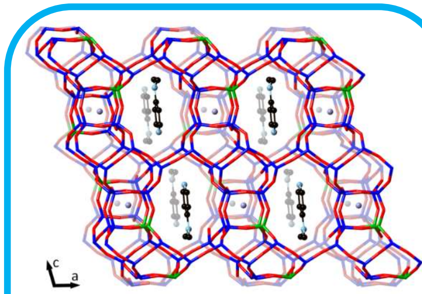
IM-18; M.O. Cichocka *et al.*, *Cryst. Growth Des.*, 2018

Outline

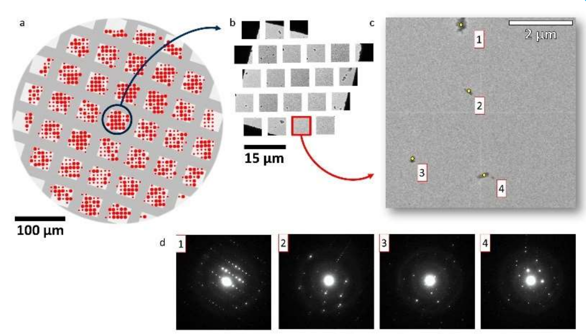
- Zeolite IM-18
  - RED + HRTEM + XRPD
- Zeolite SSZ-70
  - HRTEM + XRPD + NMR
- Serial electron diffraction
  - Structure determination
  - Phase analysis
  - Screening



SSZ-70; S. Smeets *et al.*, *J. Am. Chem. Soc.*, 2017



IM-18; M.O. Cichocka *et al.*, *Cryst. Growth Des.*, 2018

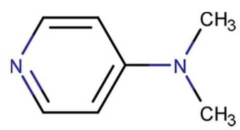


Zeolite IM-18

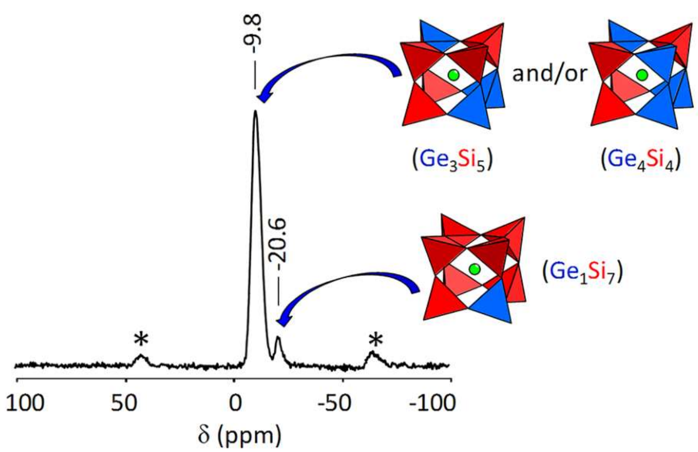
M.O. Cichocka, Y. Lorgouilloux, S. Smeets, J. Su, W. Wan, P. Caullet, N. Bats, L.B. McCusker, J.-L. Paillaud, and X. Zou. *Cryst. Growth Des.*, 18(4):2441-2451, 2018

Germanosilicate IM-18

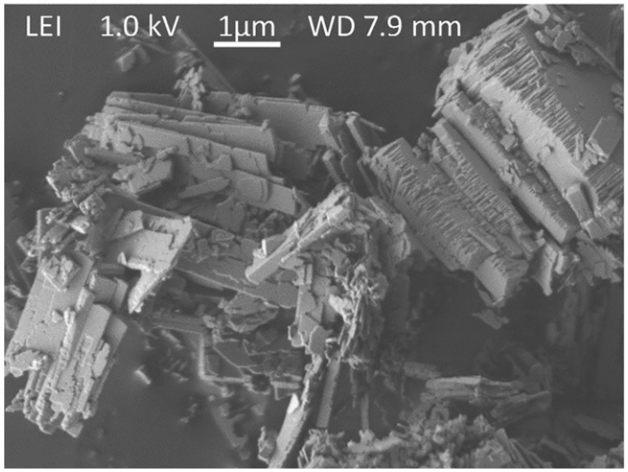
Y. Lorgouilloux, *et al.* French patent 2,923,477 (2007)



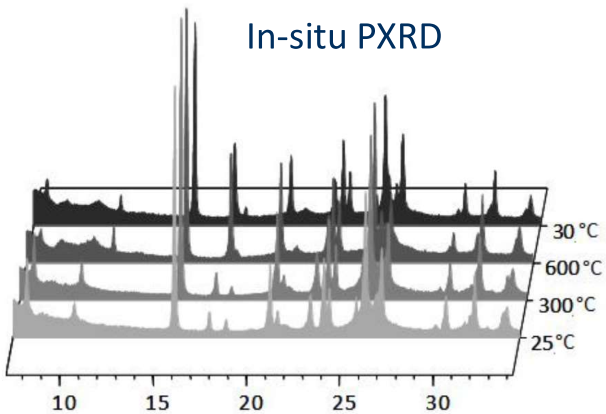
4-Dimethylaminopyridine (DMAP)



^{19}F MAS-NMR

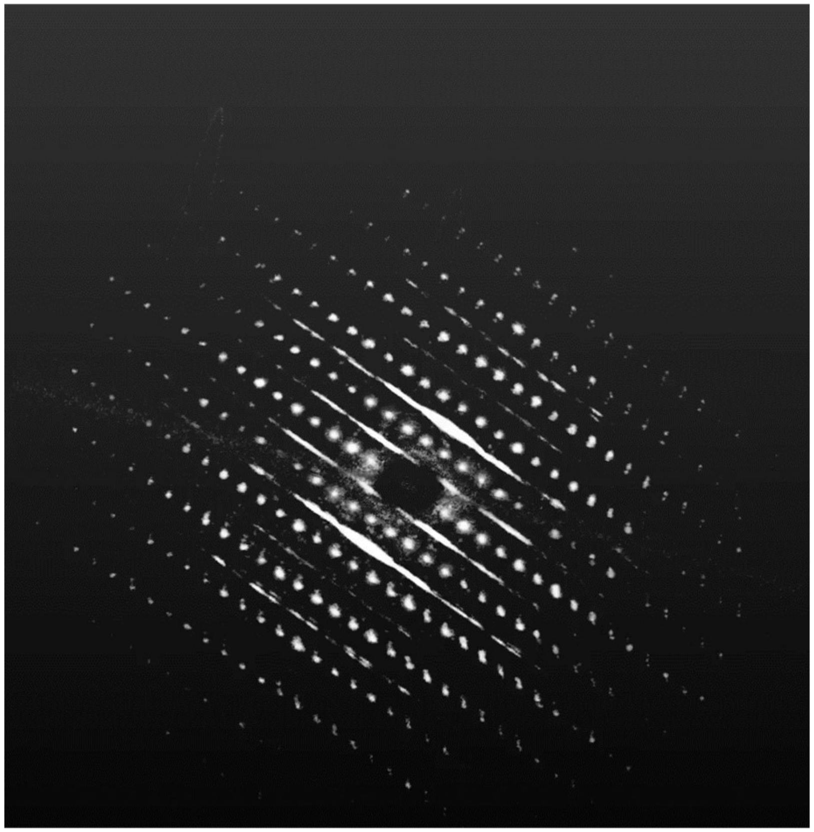


In-situ PXRD



M. O. Cichocka *et al.*, *Cryst. Growth Des.*, 18(4):2441-2451, 2018

Rotation electron diffraction



Tilt range (°)	119.46 (-66.83 to 52.63)
Tilt step (°)	0.2°
Exposure time/frame (s)	1.0
No. of frames	649
Crystal size (µm)	0.66 x 0.74
Resolution (Å)	1.05
Completeness (%)	89.9
Reflections	1265

Index Bragg spots

Orthorhombic $Imma$ / $Im2a$

a = 5.31 Å — α = 89.79°

b = 15.07 Å — β = 88.81°

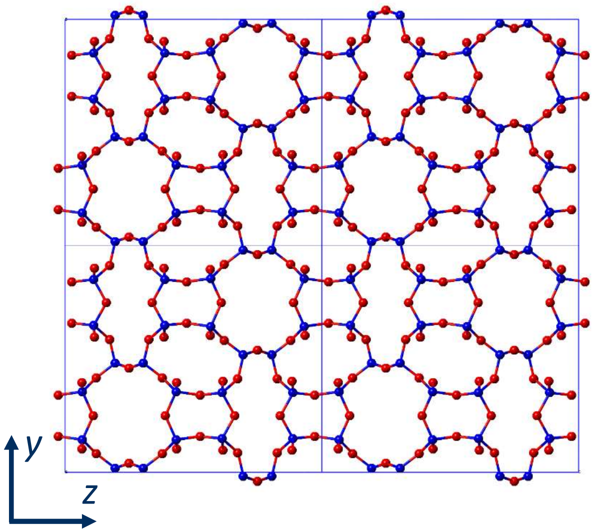
c = 17.06 Å — γ = 90.35°

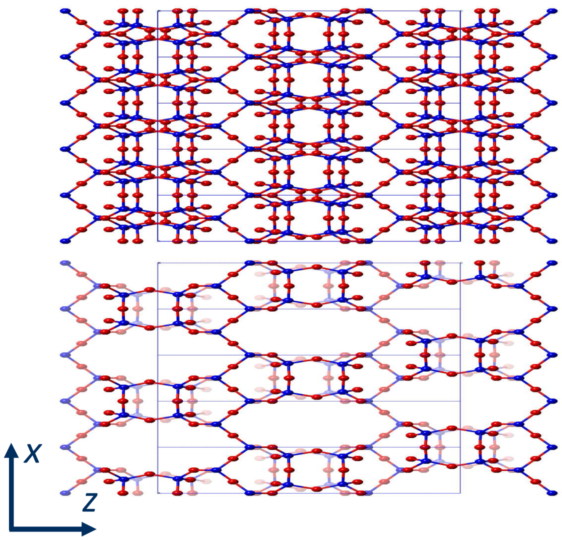
$hkl: h + k + l = 2n$

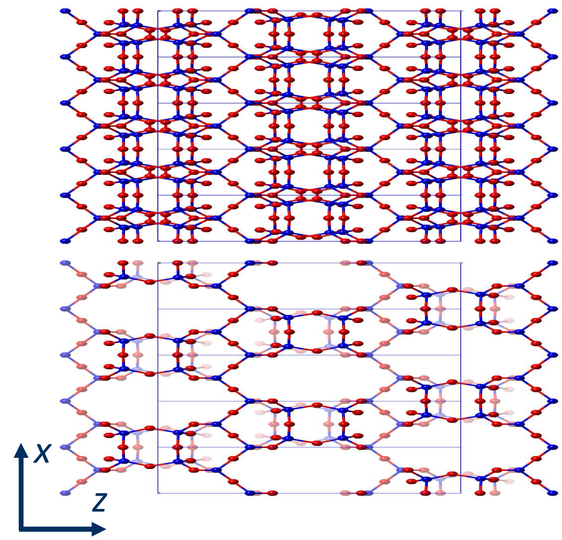
$hk0: h = 2n, k = 2n$

M. O. Cichocka *et al.*, *Cryst. Growth Des.*, 18(4):2441-2451, 2018

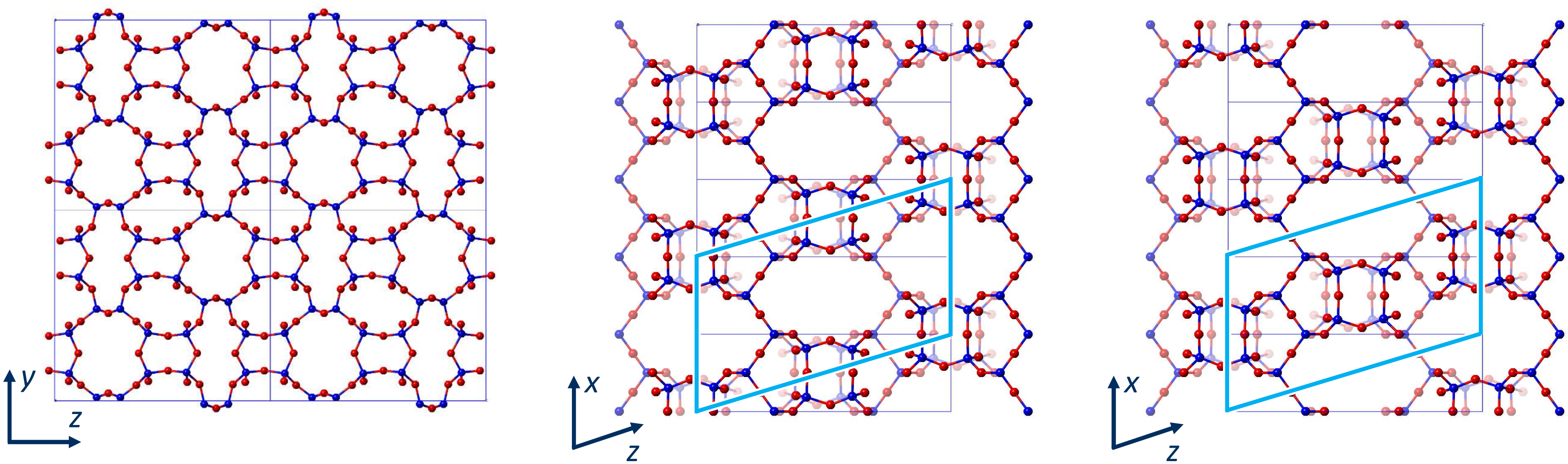
Average framework structure from SHELXS







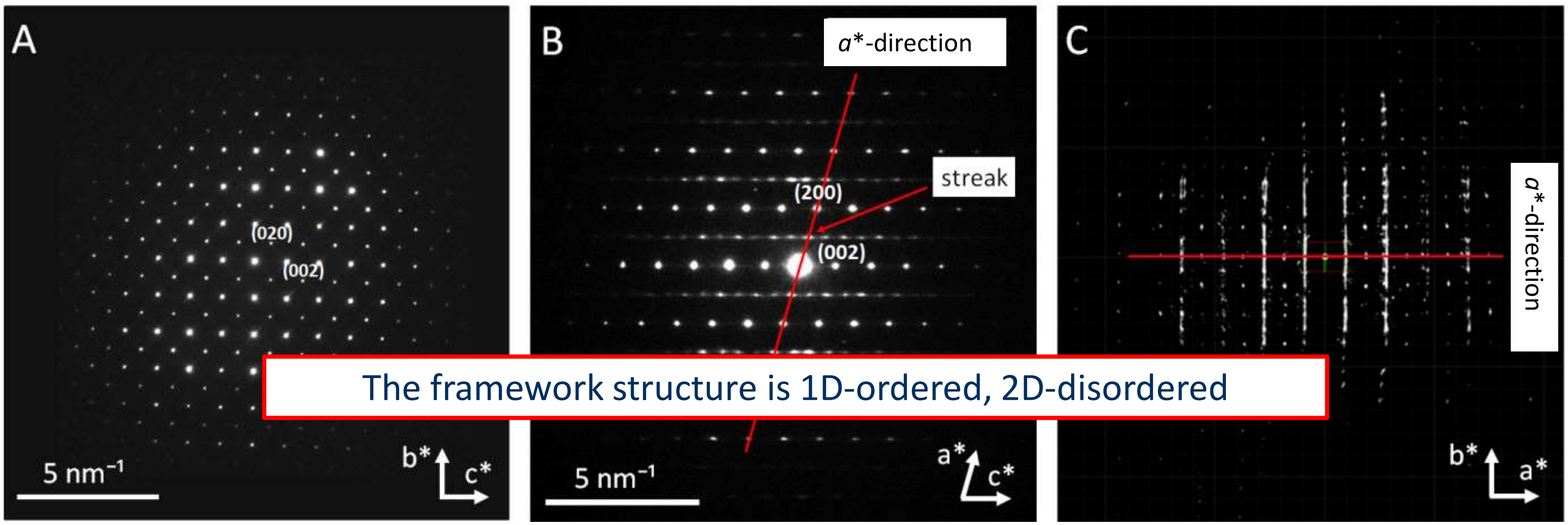
Average framework structure from SHELXS



Monoclinic $P2_1/m$

a = 10.336 Å, b = 14.984 Å, c = 17.734 Å, β = 106.94°

Selected area electron diffraction



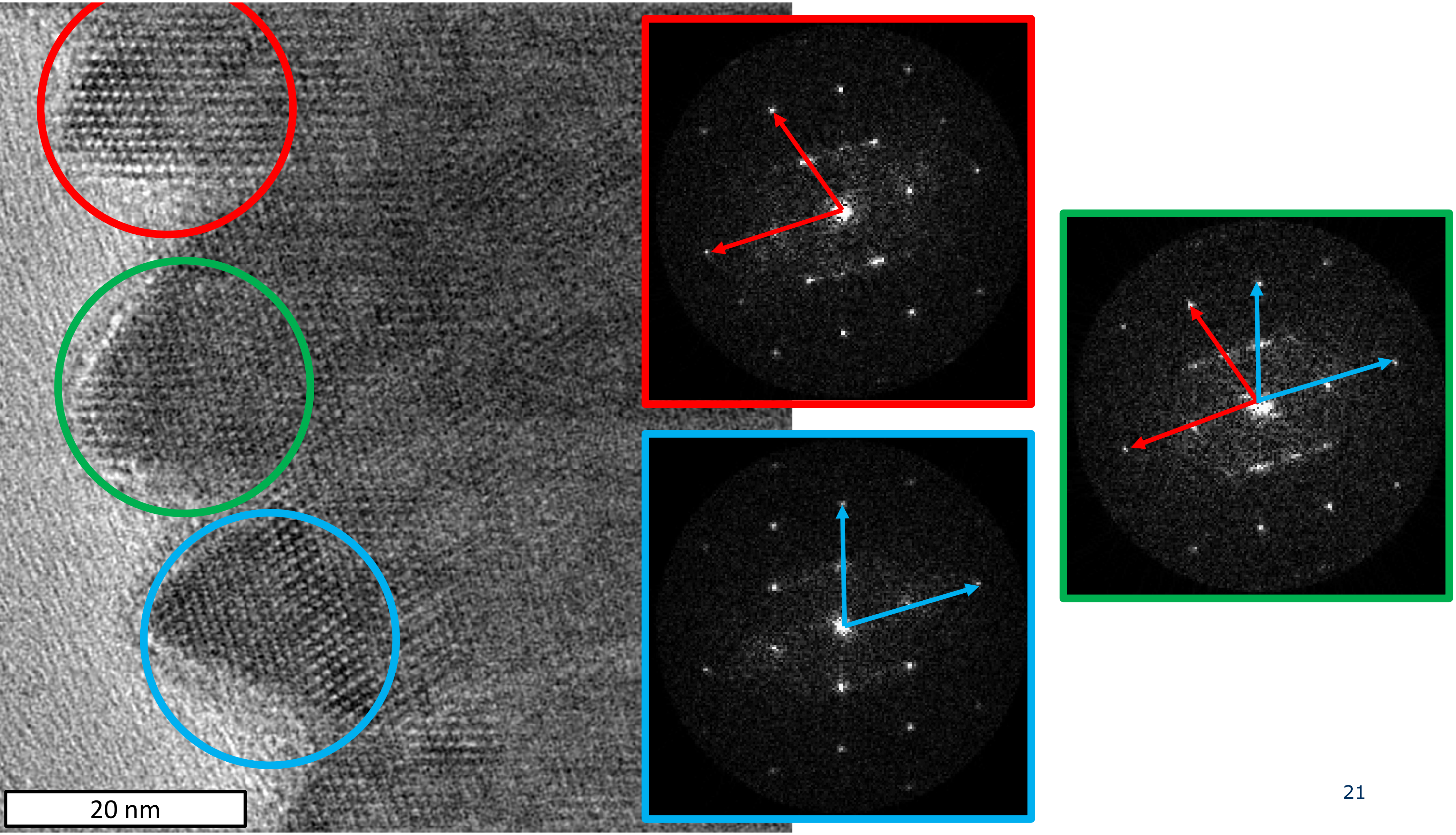
The framework structure is 1D-ordered, 2D-disordered

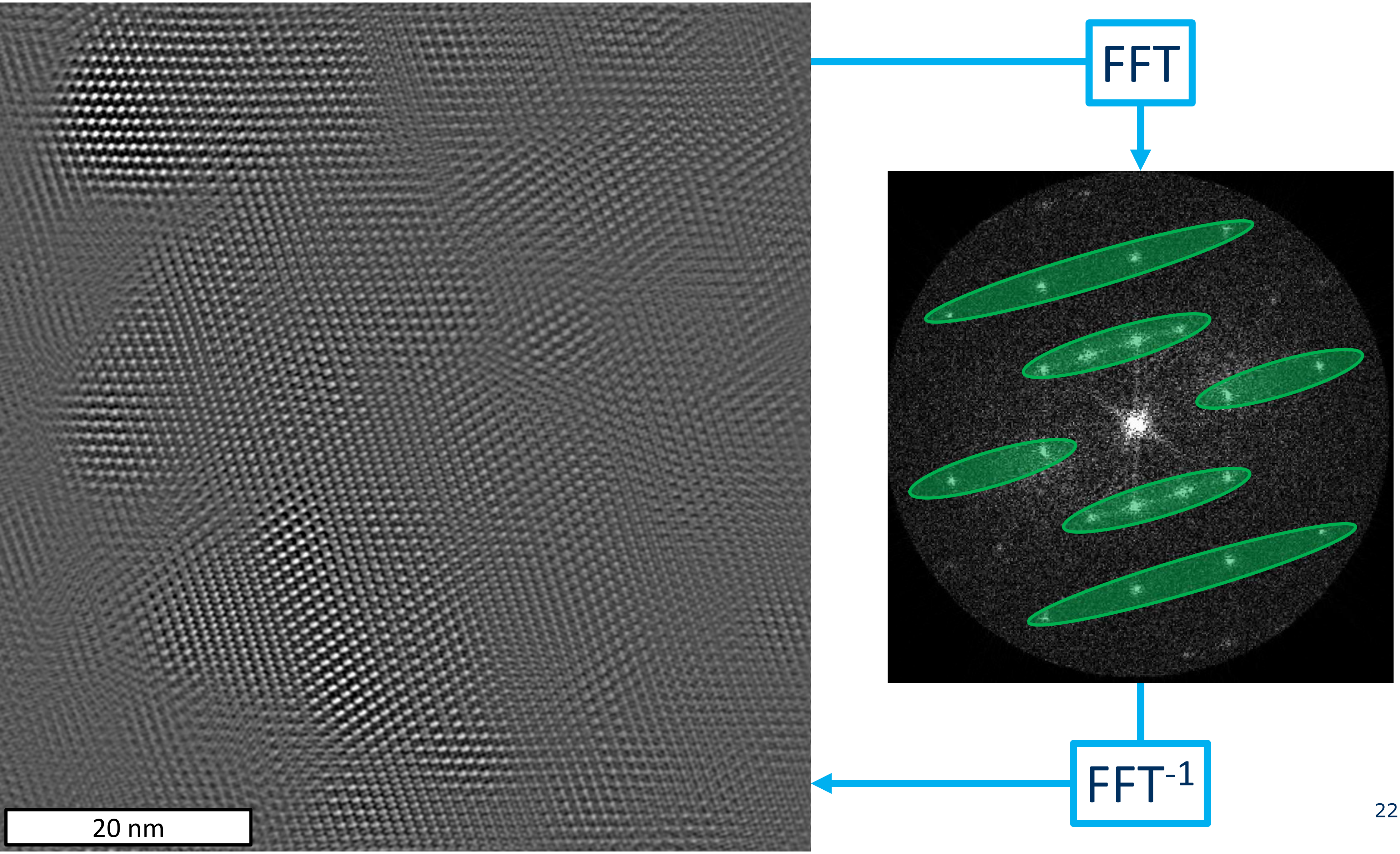
[100] [010] [001]

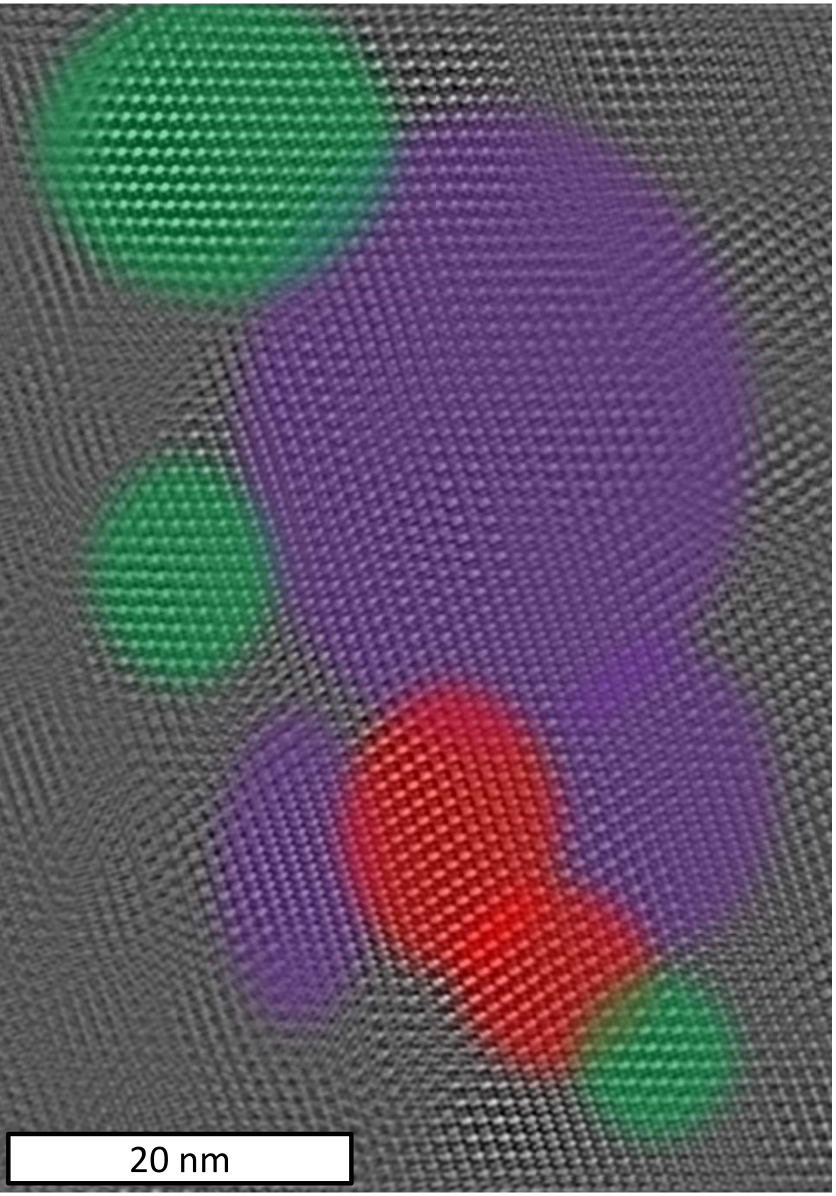
Monoclinic $P2_1/m$

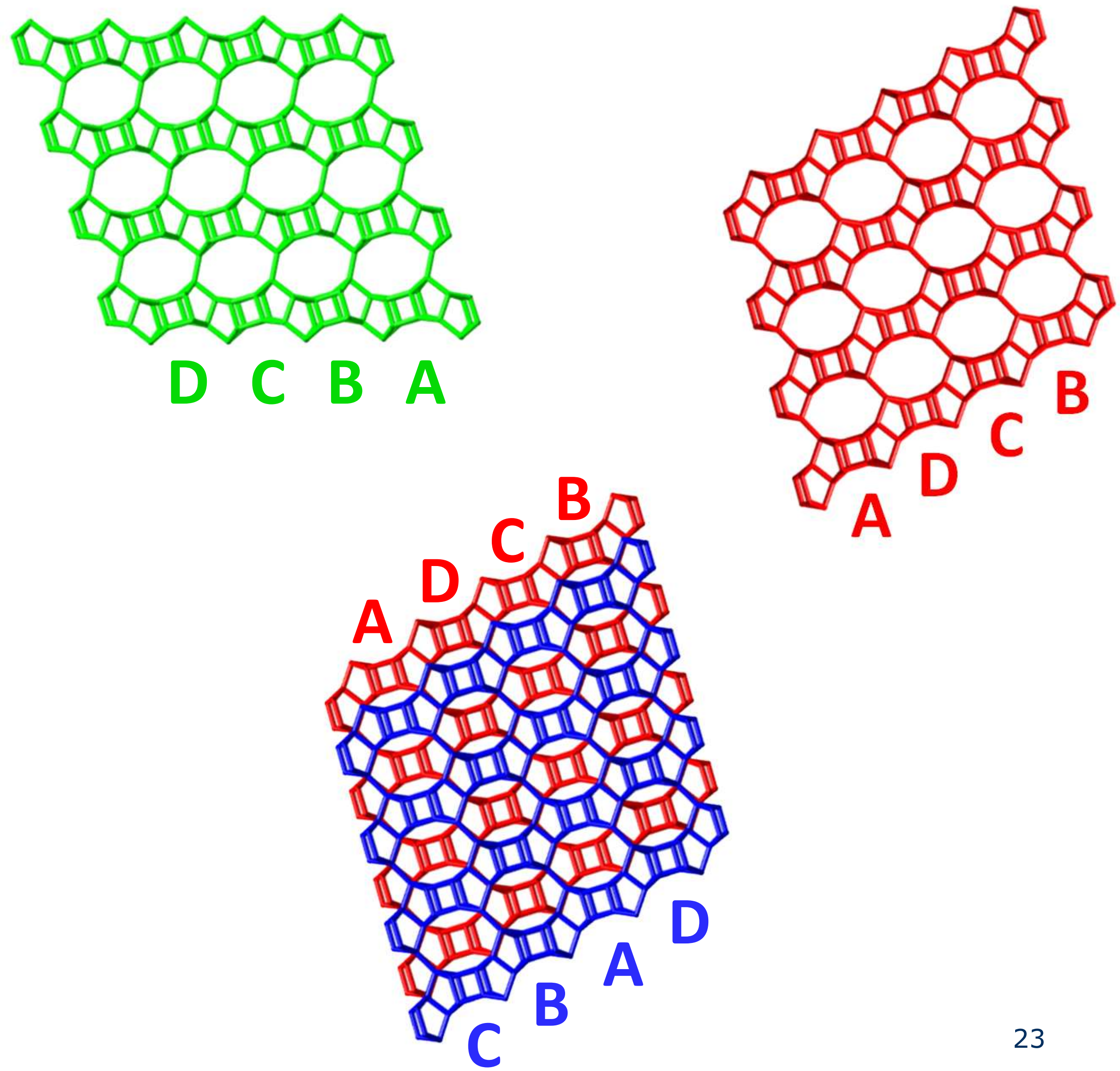
a = 10.336 Å, *b* = 14.984 Å, *c* = 17.734 Å, *β* = 106.94°

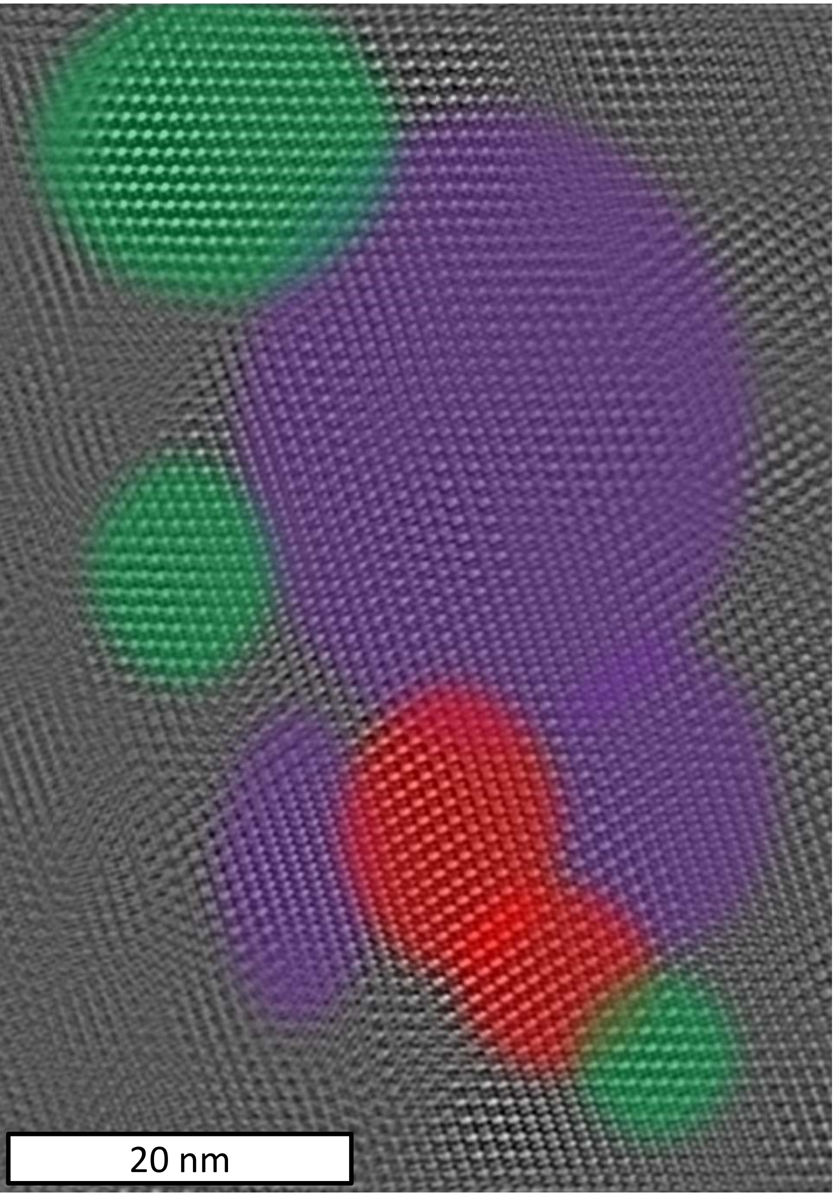
M. O. Cichocka *et al.*, *Cryst. Growth Des.*, 18(4):2441-2451, 2018

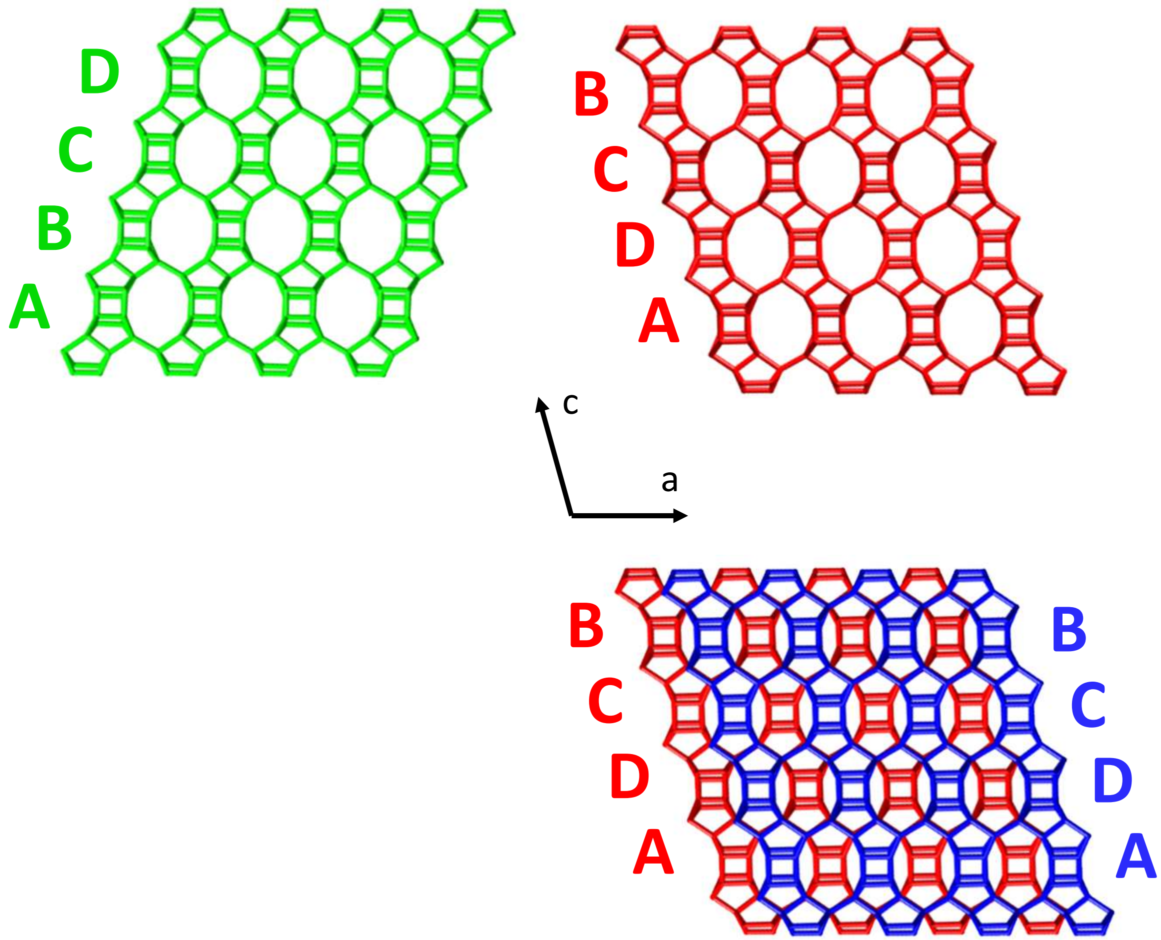

20 nm


FFT
FFT-1
20 nm

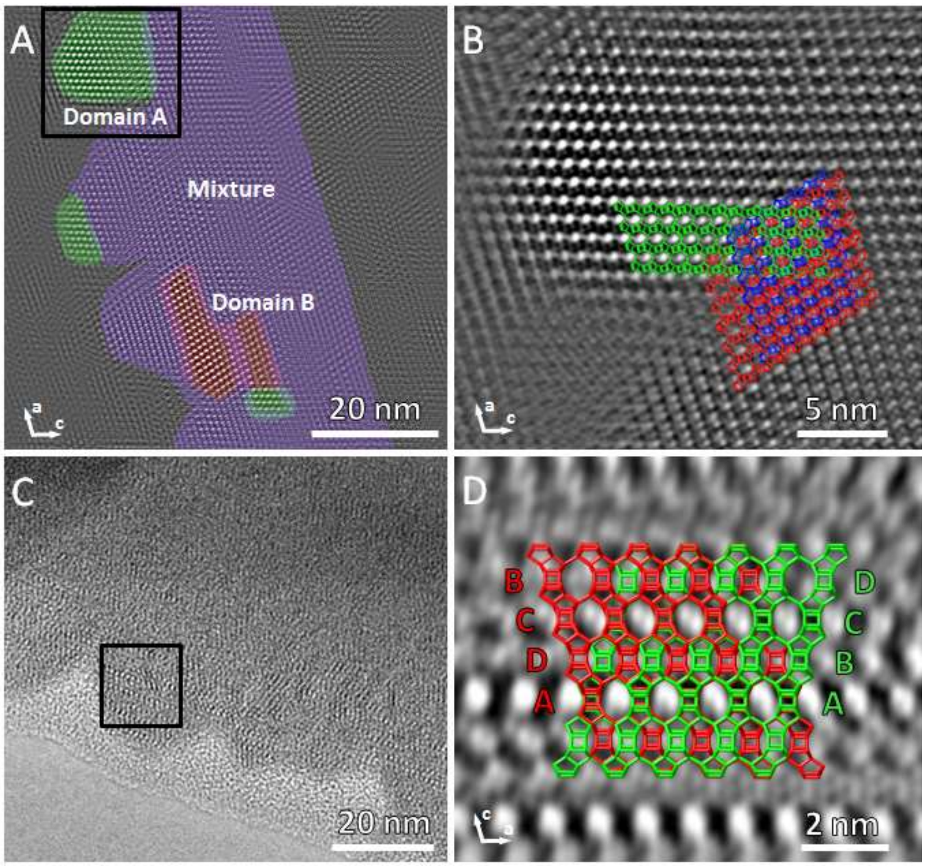

20 nm

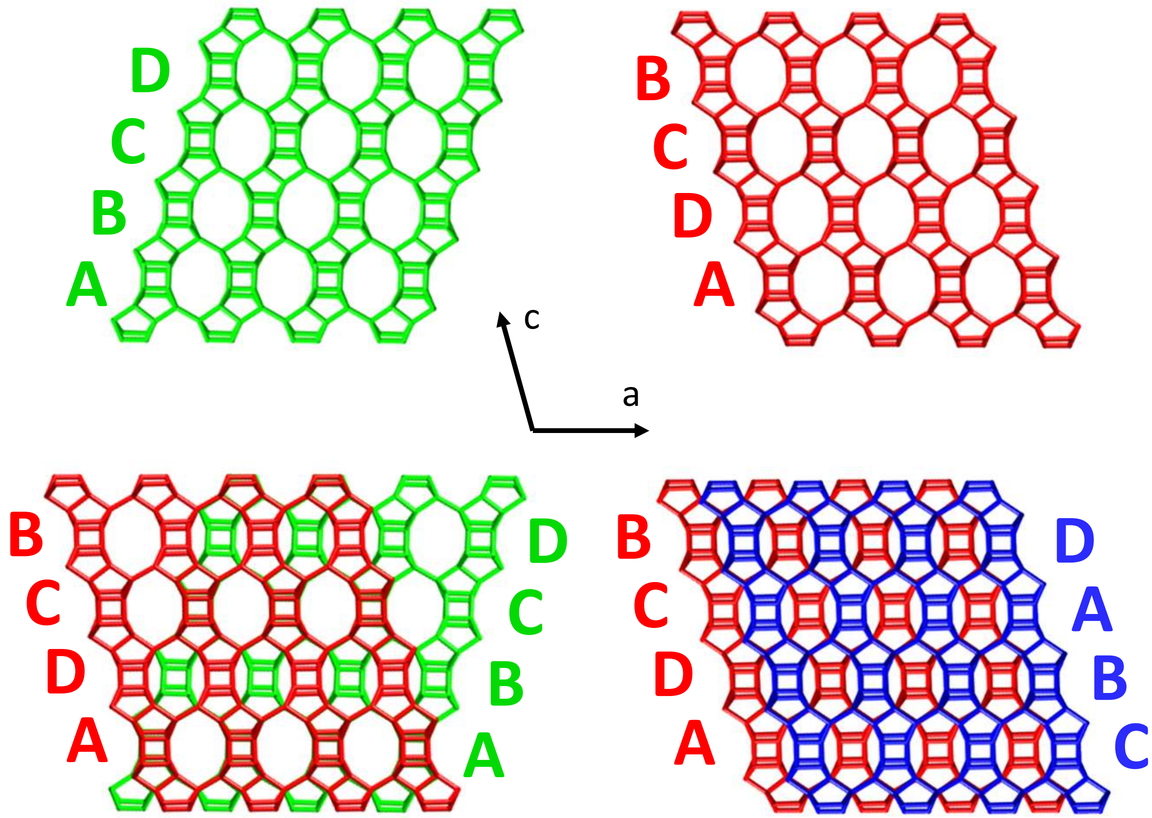

D C B A
A D C B
A D C B
C B A D


20 nm


D
C
B
A
B
C
D
A
c
a
B
C
D
A
B
C
D
A

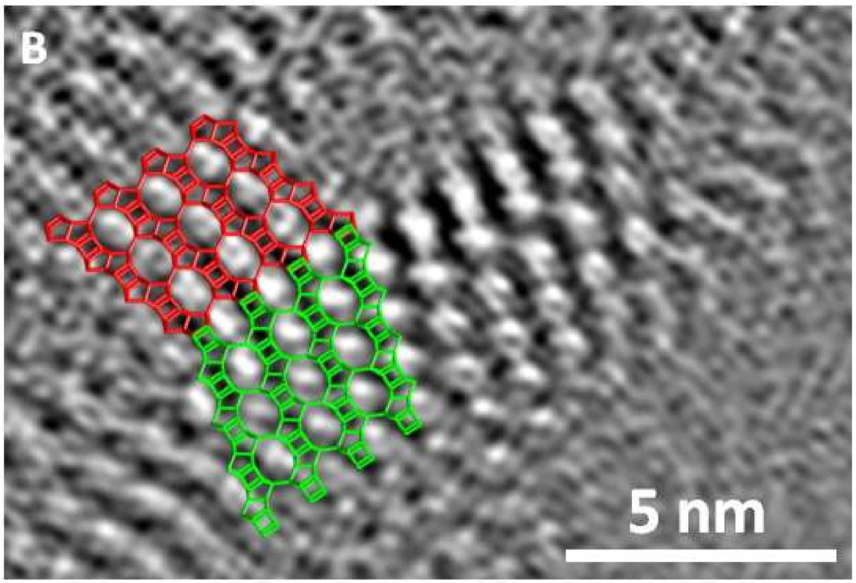
HRTEM

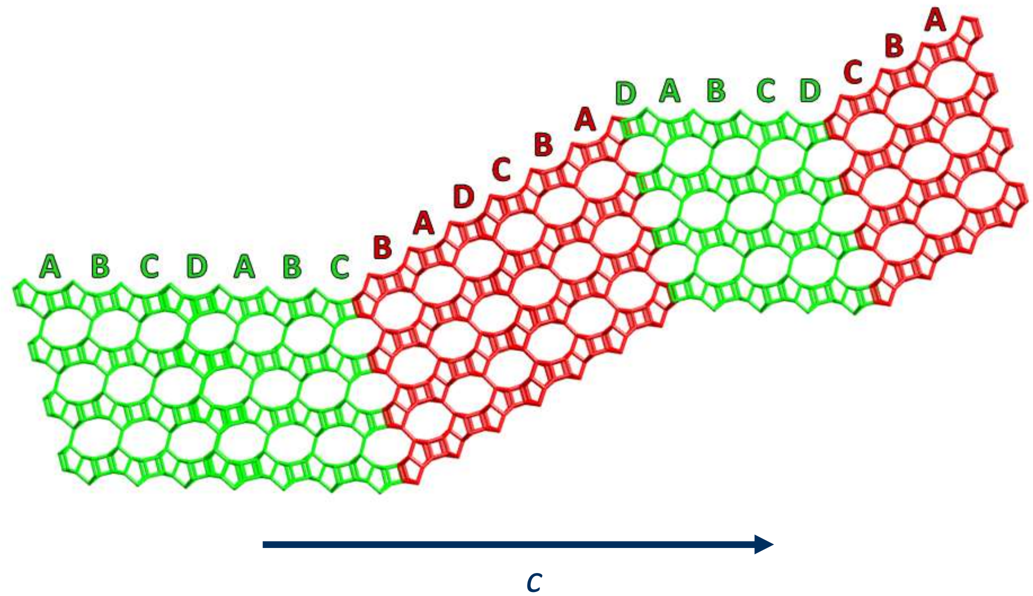




M. O. Cichocka *et al.*, *Cryst. Growth Des.*, 18(4):2441-2451, 2018

HRTEM



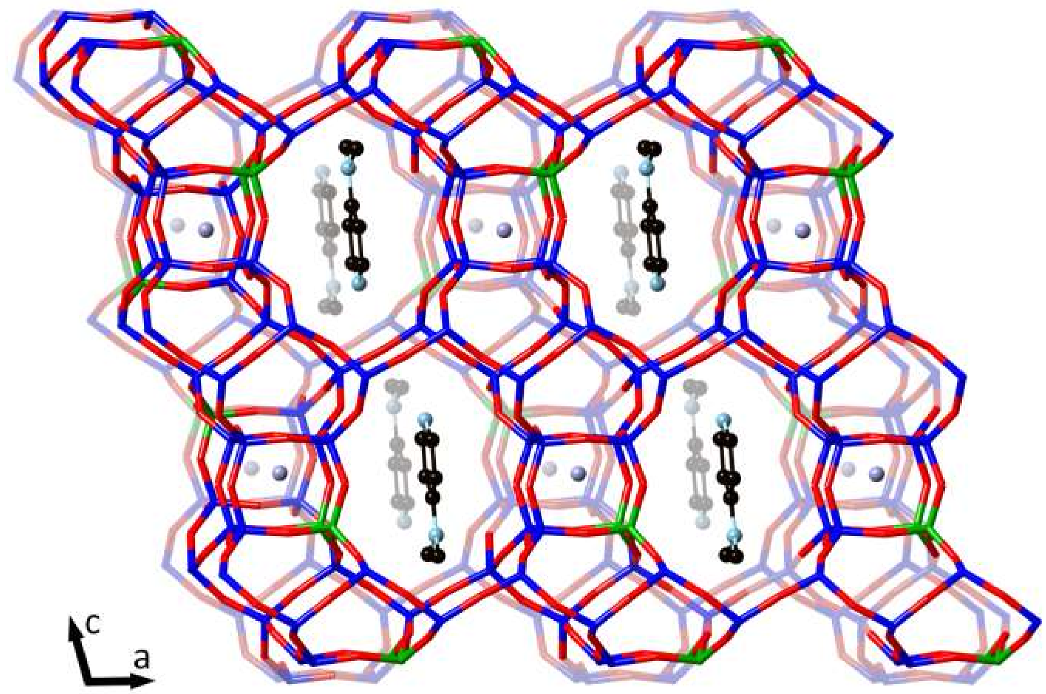


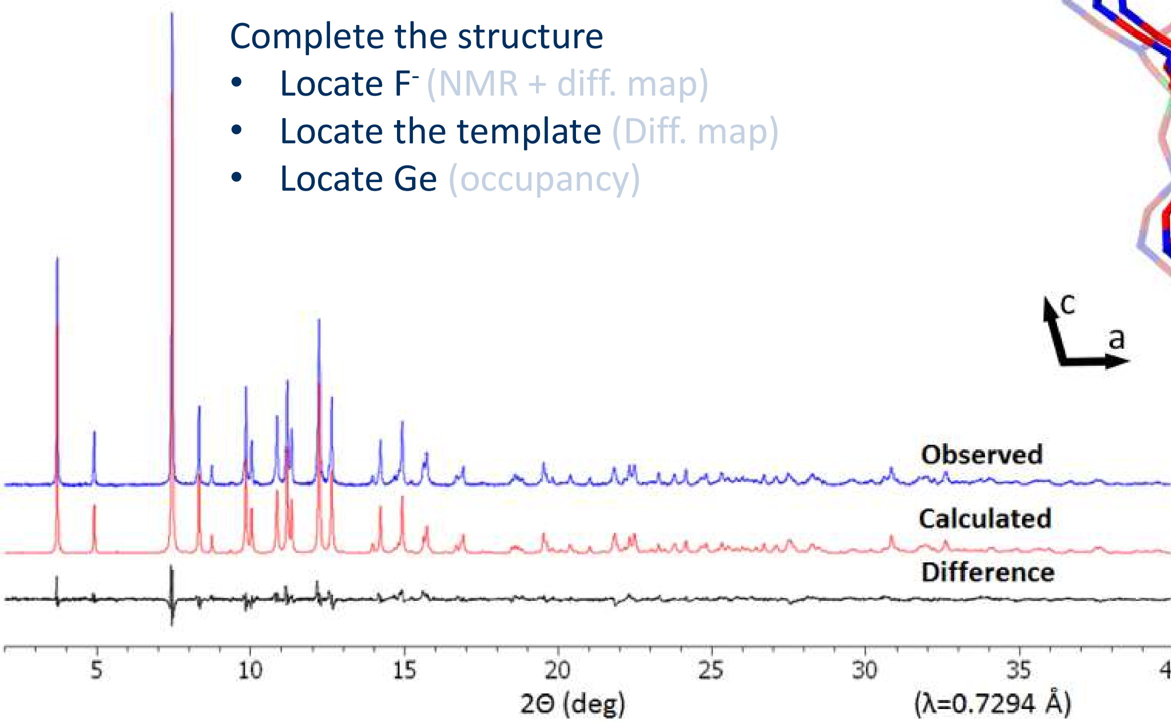
M. O. Cichocka *et al.*, *Cryst. Growth Des.*, 18(4):2441-2451, 2018

Structure refinement

Complete the structure

- Locate F^- (NMR + diff. map)
- Locate the template (Diff. map)
- Locate Ge (occupancy)



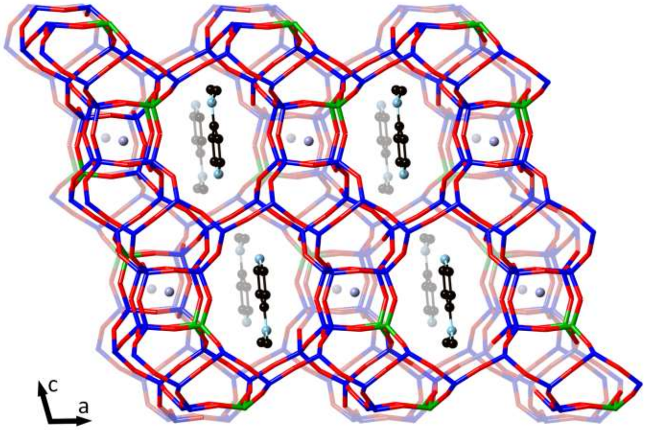


$P2_1/m$
a = 10.5089(5) Å
b = 14.9425(5) Å
c = 17.7775(7) Å
β = 107.323(4)°

M. O. Cichocka *et al.*, *Cryst. Growth Des.*, 18(4):2441-2451, 2018

Summary IM-18

- Structure of IM-18 determined by combining methods
  - RED → Average structure
  - SAED → Disorder
  - HRTEM → Short-range order
  - XRPD → Structure completion
    → Model validation



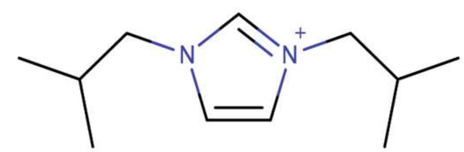
- New zeolite framework topology

- Experimental evidence for 2D stacking disorder

Zeolite SSZ-70

S. Smeets, Z.J. Berkson, D. Xie, S.I. Zones, W. Wan, X. Zou, M.-F. Hsieh, B.F. Chmelka, L.B. McCusker, and C. Baerlocher. *J. Am. Chem. Soc.*, 139(46):16803-16812, 2017

Zeolite SSZ-70

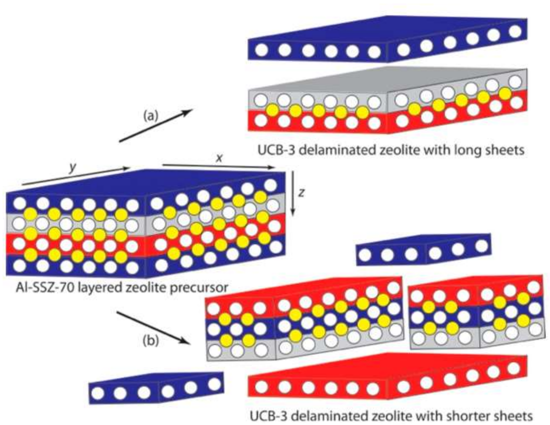


Stacey Zones and Alan Burton, US Patent 7,108,843 B2 (2006)
Molecular sieve SSZ-70 composition of matter and synthesis thereof

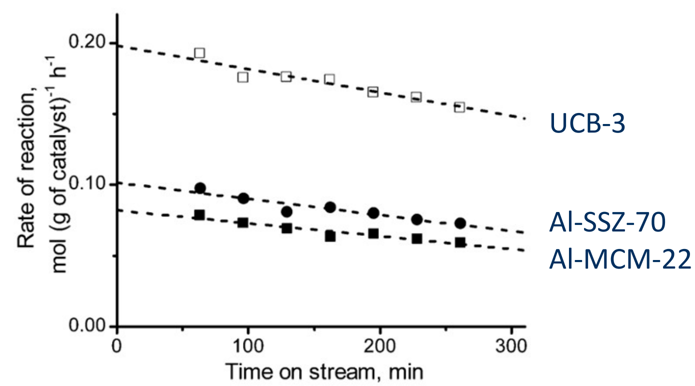
Pure silicate
Borosilicate
Aluminosilicate

→ Heat treatment >500°C → Calcined SSZ-70

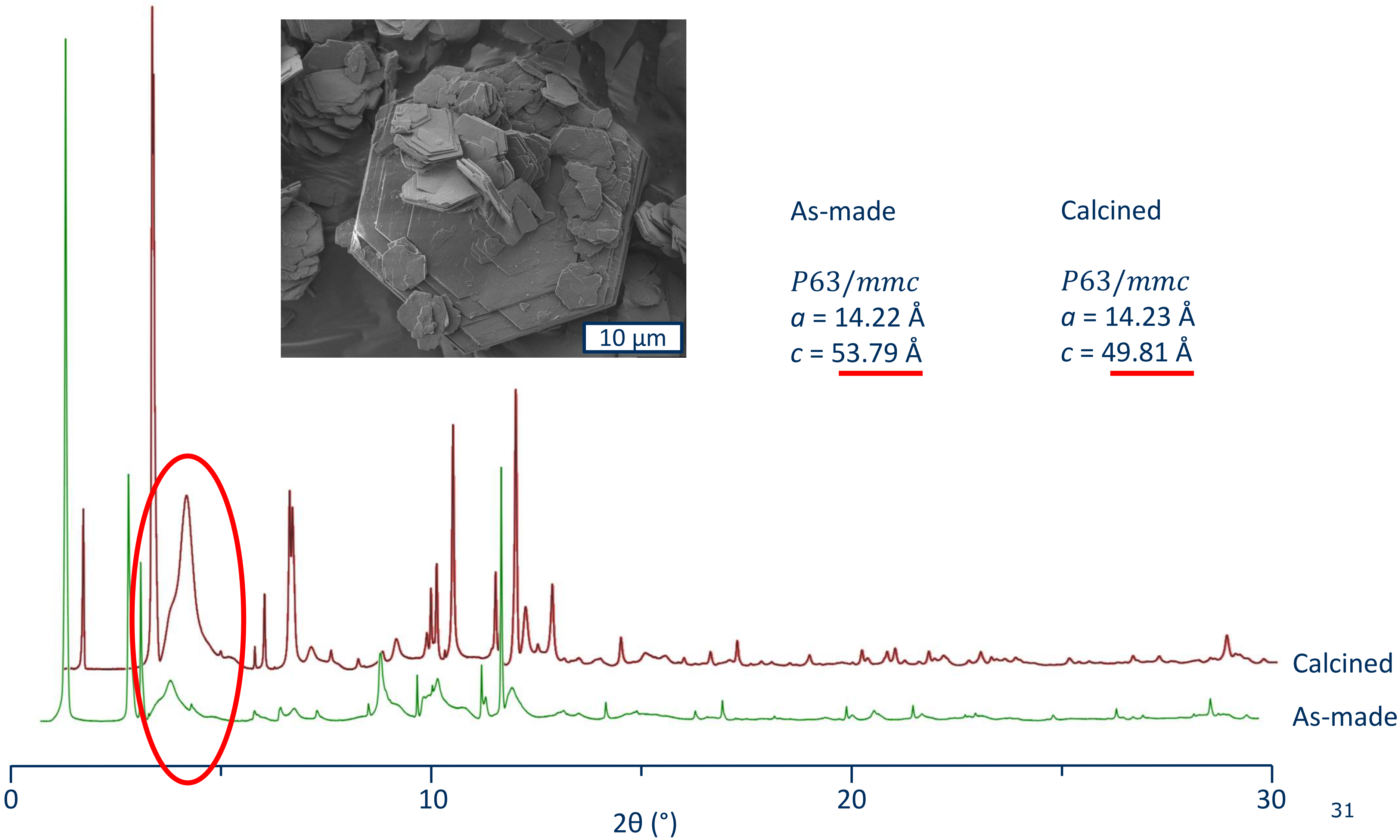
→ Delamination → UCB-3 (Al) / UCB-4 (B)



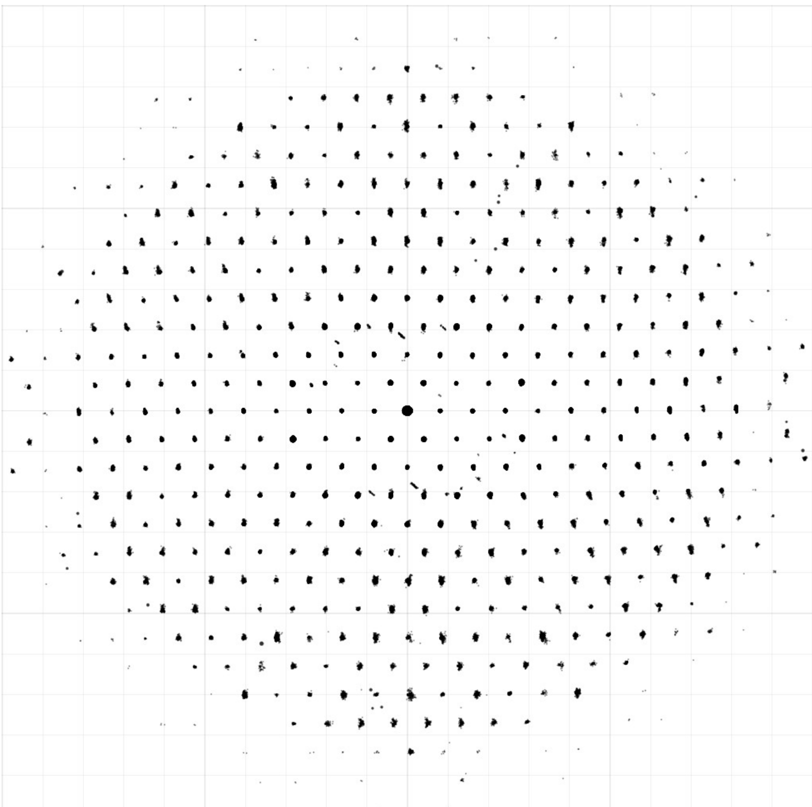
Catalysis: aromatic alkylation



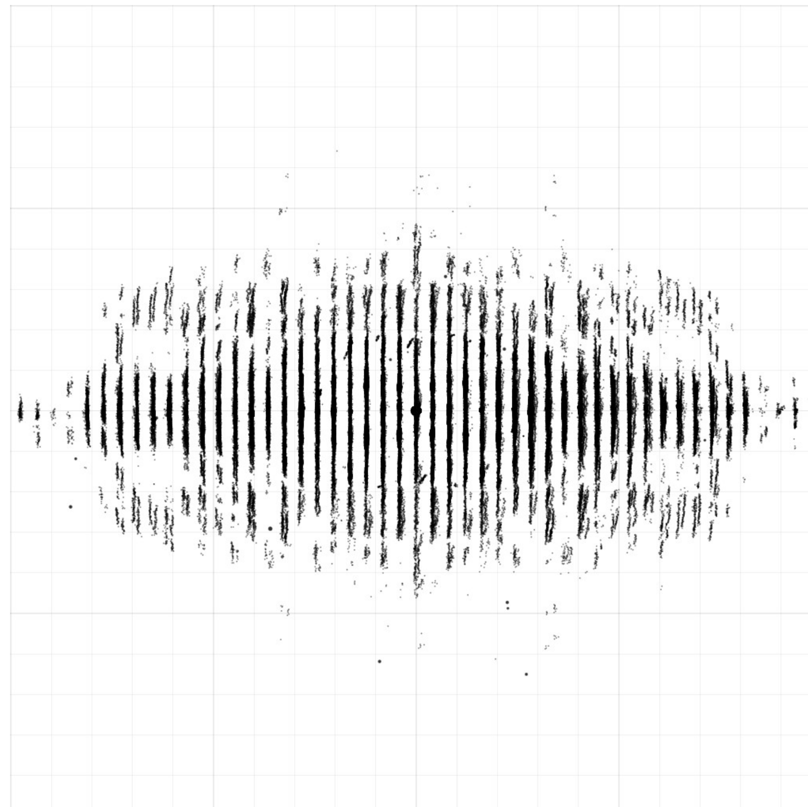
Runnebaum *et al.*, **2014**, *ACS Catal.*, 4, 2364


10 µm
As-made
$P63/mmc$
a = 14.22 Å
c = 53.79 Å
Calcined
$P63/mmc$
a = 14.23 Å
c = 49.81 Å
Calcined
As-made
0
10
20
30
2θ (°)

Electron diffraction (as-made)

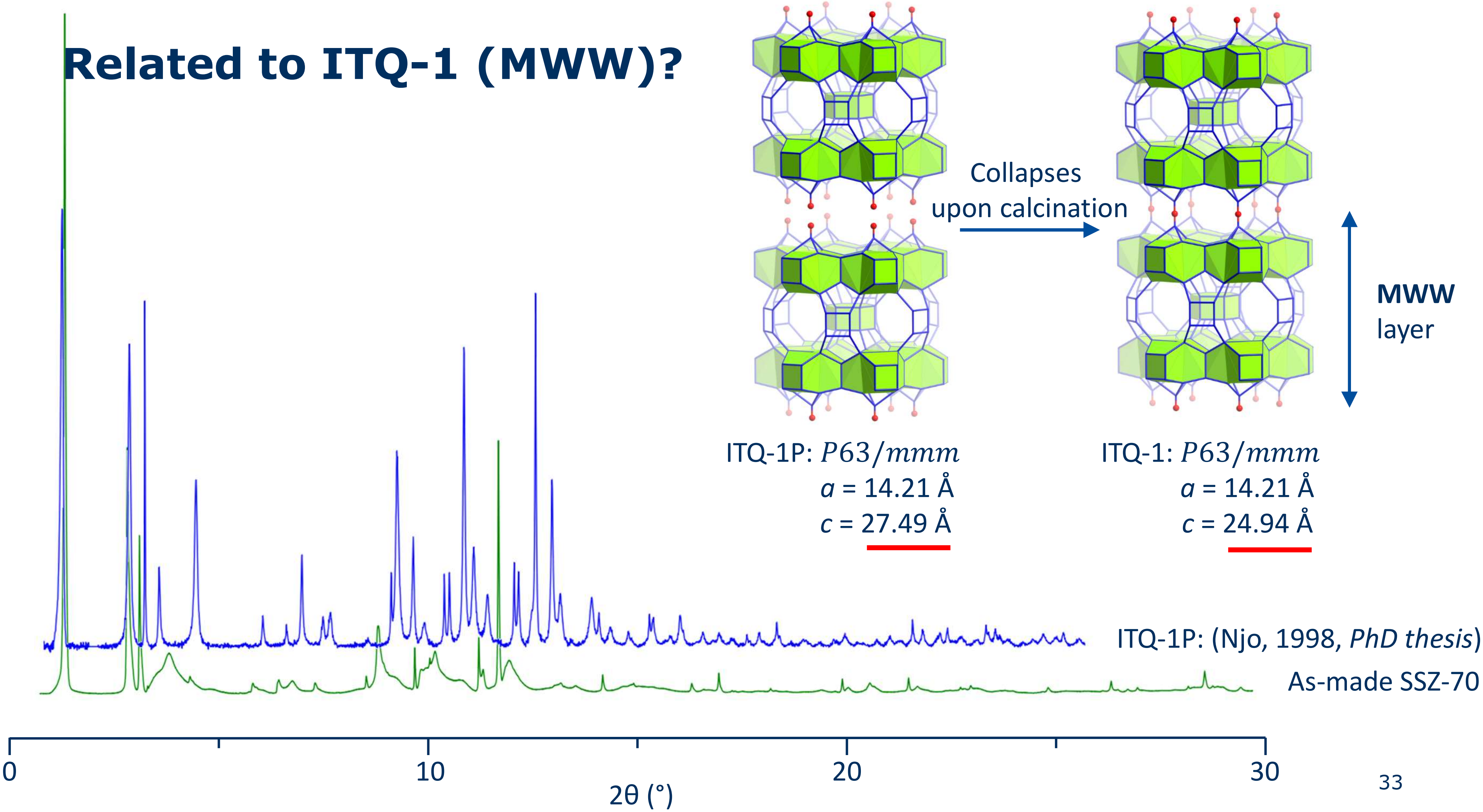


Along [001]



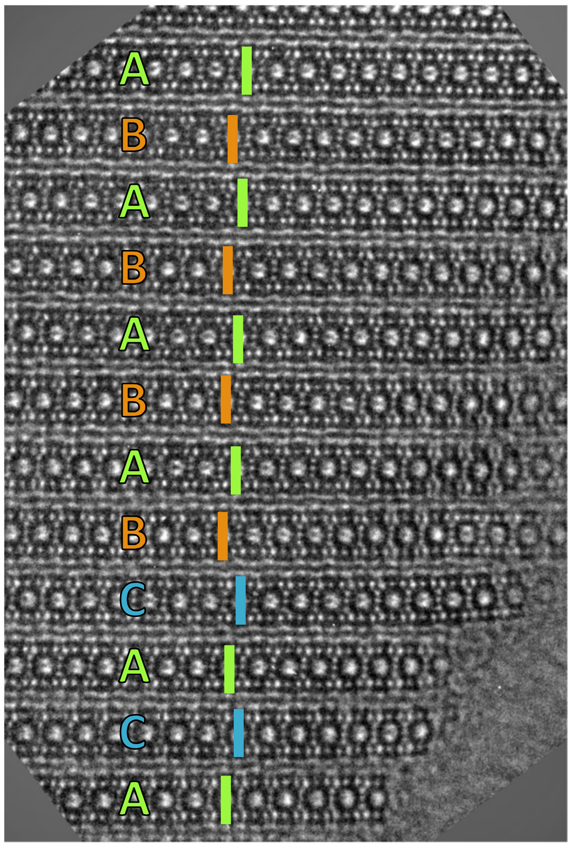
Along [100]

Related to ITQ-1 (MWW)?



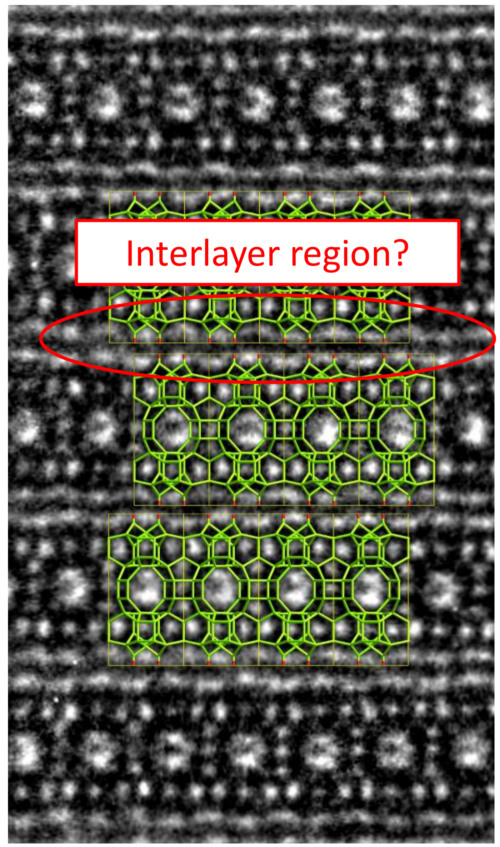
HRTEM (as-made)

Stacking disorder along [001]

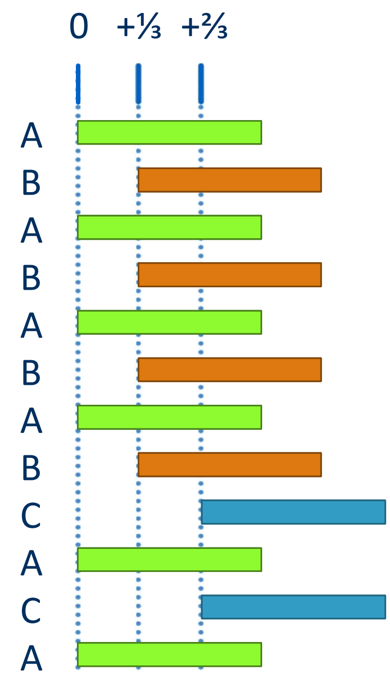


Collected by Wei Wan, Stockholm University, SE

MWW-layers



Stacking faults

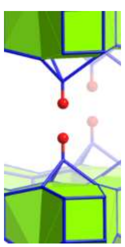


SSZ-70

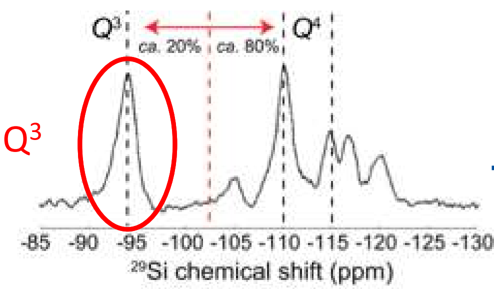
Solid-state ^{29}Si MAS NMR

As-made

Calcined

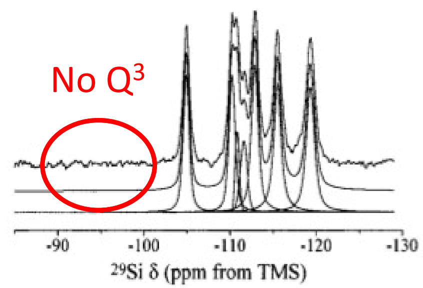


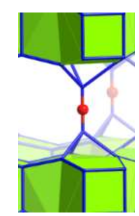
20% Q^3



ITQ-1

No Q^3





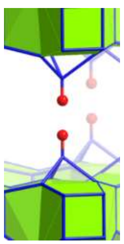
Hsieh, Aronson and Chmelka (2014)

Archer *et al.*, **2010,** *Micropor. Mesopor. Mat.*, 130, 255
Camblor *et al.*, **1998**, *J. Phys. Chem. B*, 102, 44

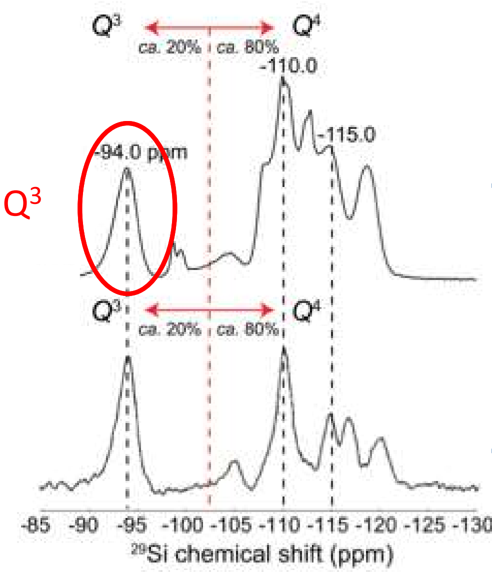
Solid-state ^{29}Si MAS NMR

As-made

Calcined



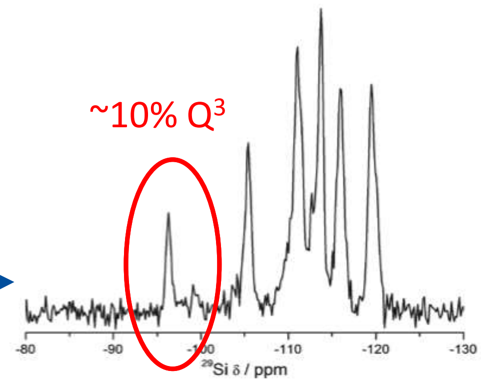
20% Q^3

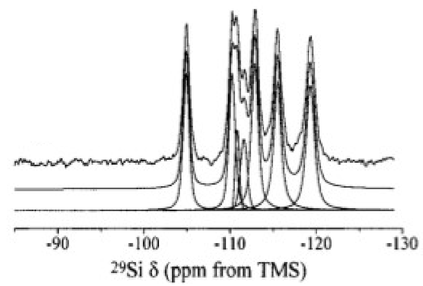


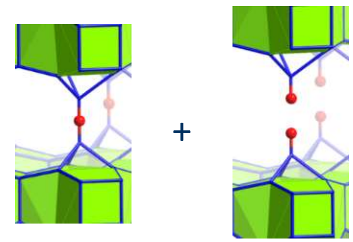
SSZ-70

ITQ-1

~10% Q^3



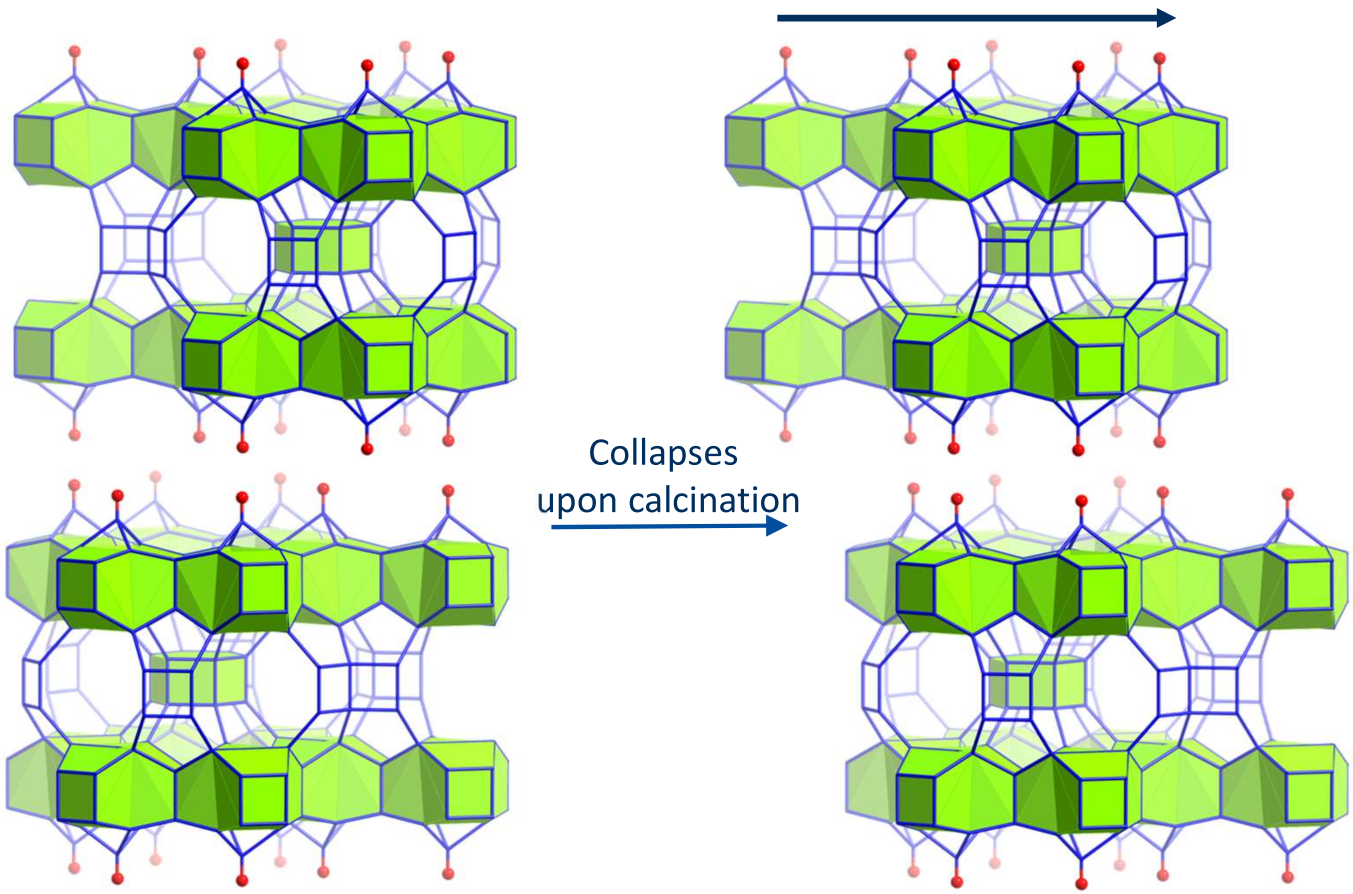




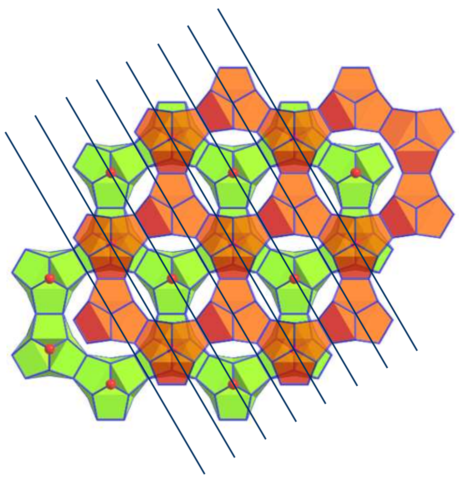
Hsieh, Aronson and Chmelka (2014)

Archer *et al.*, **2010**, *Micropor. Mesopor. Mat.*, 130, 255
Camblor *et al.*, **1998**, *J. Phys. Chem. B*, 102, 44

Model for SSZ-70

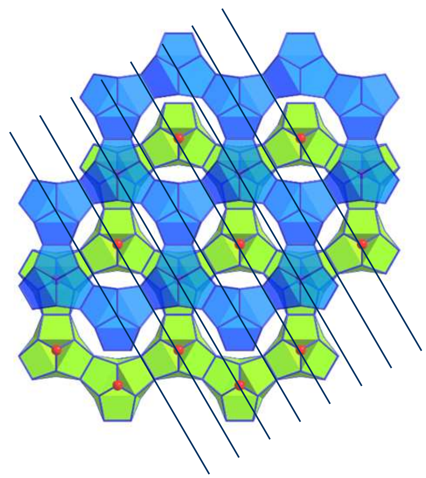


Disorder model



$x+\frac{2}{3},\ y+\frac{1}{3}$

P(A → B) = 50%

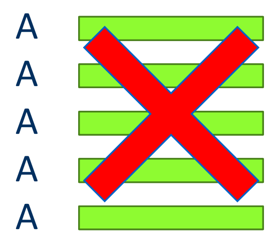


$x+\frac{1}{3},\ y+\frac{2}{3}$

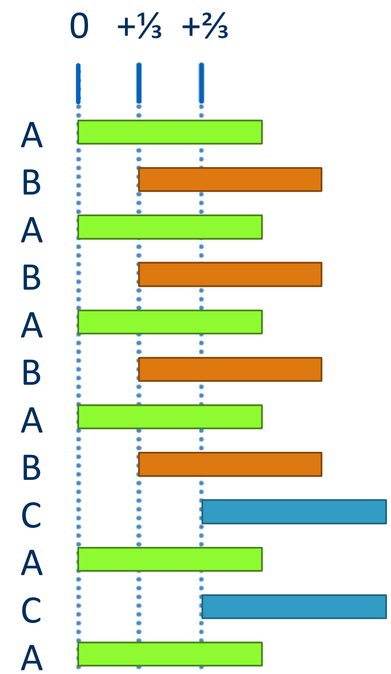
P(A → C) = 50%

*Random arrangement of **MWW** layers*

P(A → A) = 0%
P(A → B) = 50%
P(A → C) = 50%

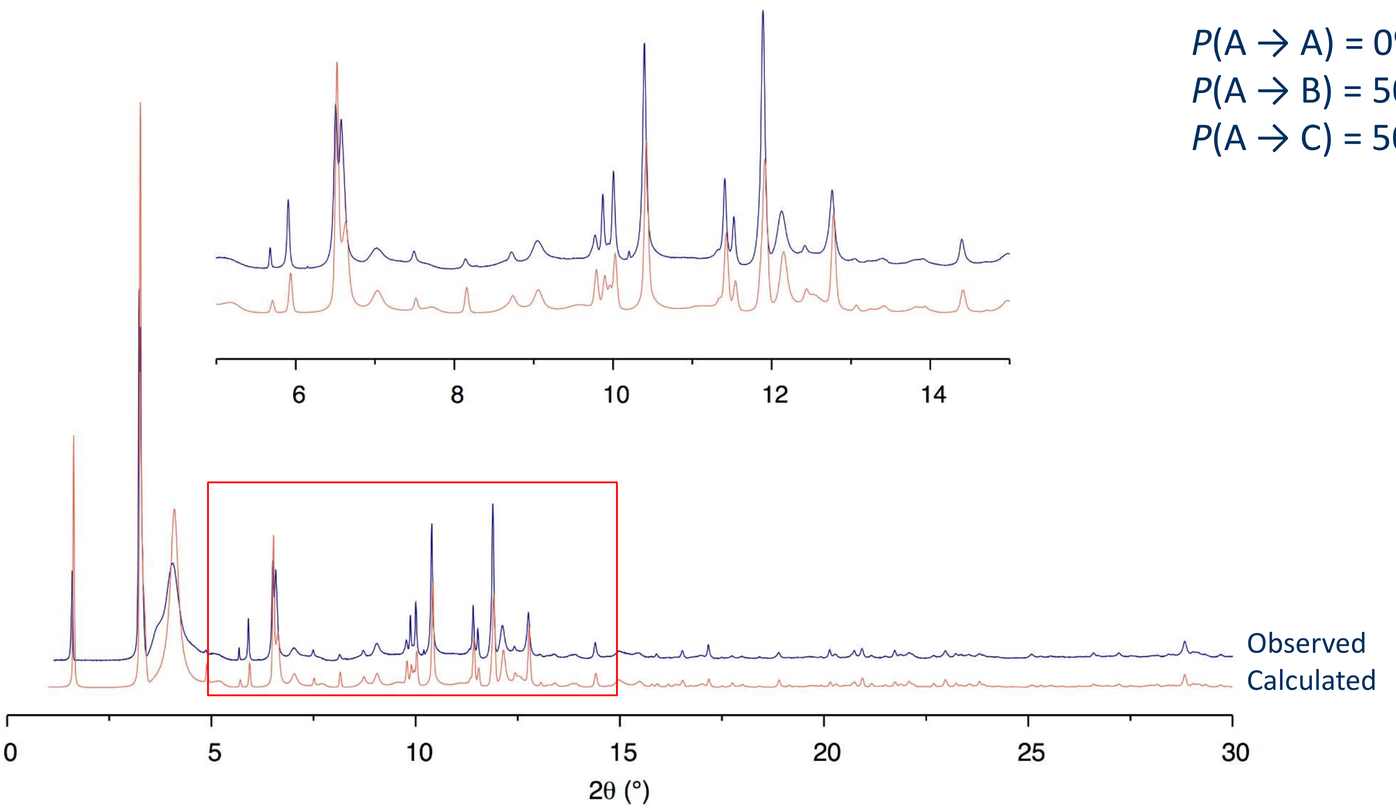


ITQ-1



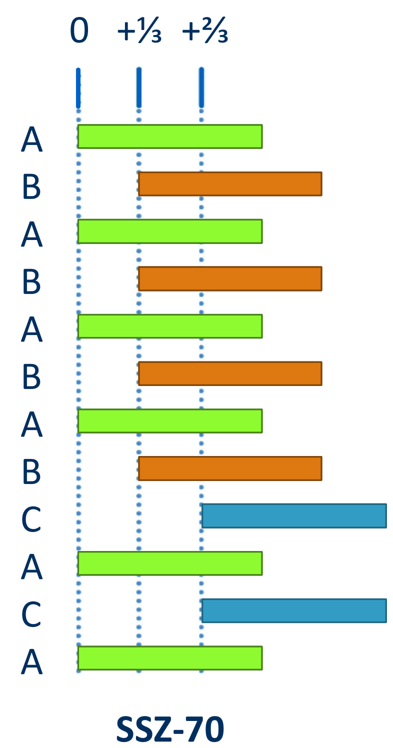
SSZ-70

Simulations using DiFFaX



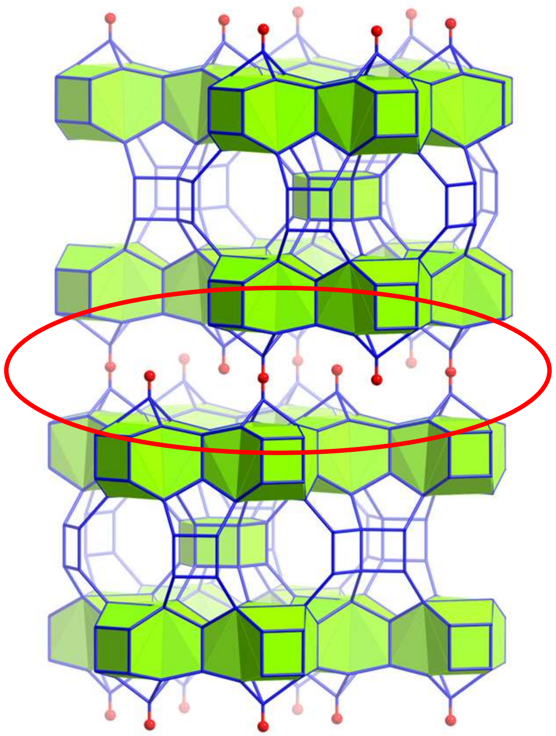
*Random arrangement of **MWW** layers*

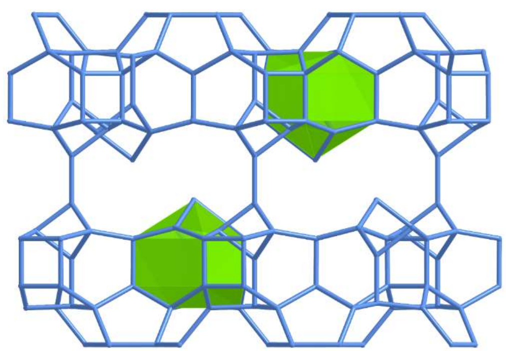
$P(A \rightarrow A) = 0\%$
$P(A \rightarrow B) = 50\%$
$P(A \rightarrow C) = 50\%$

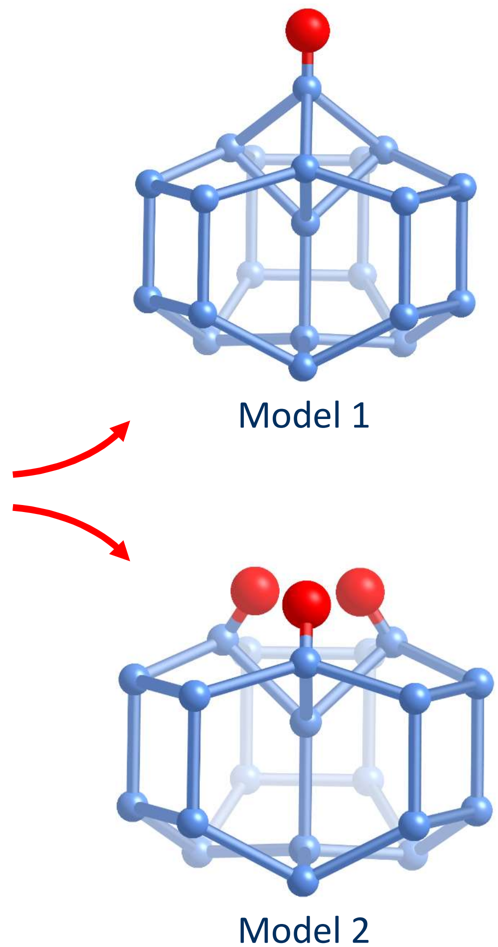


DiFFaX: Traecy *et al.*, **1991**, *Proc. R. Soc. Lond. A*, 433, 499

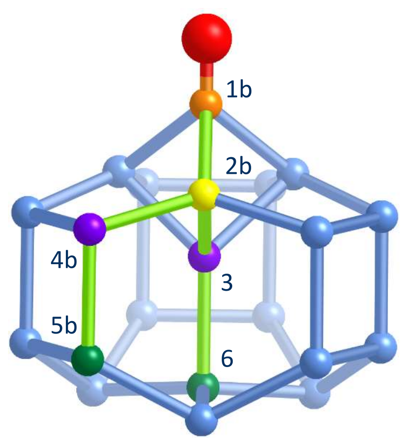
Interlayer region



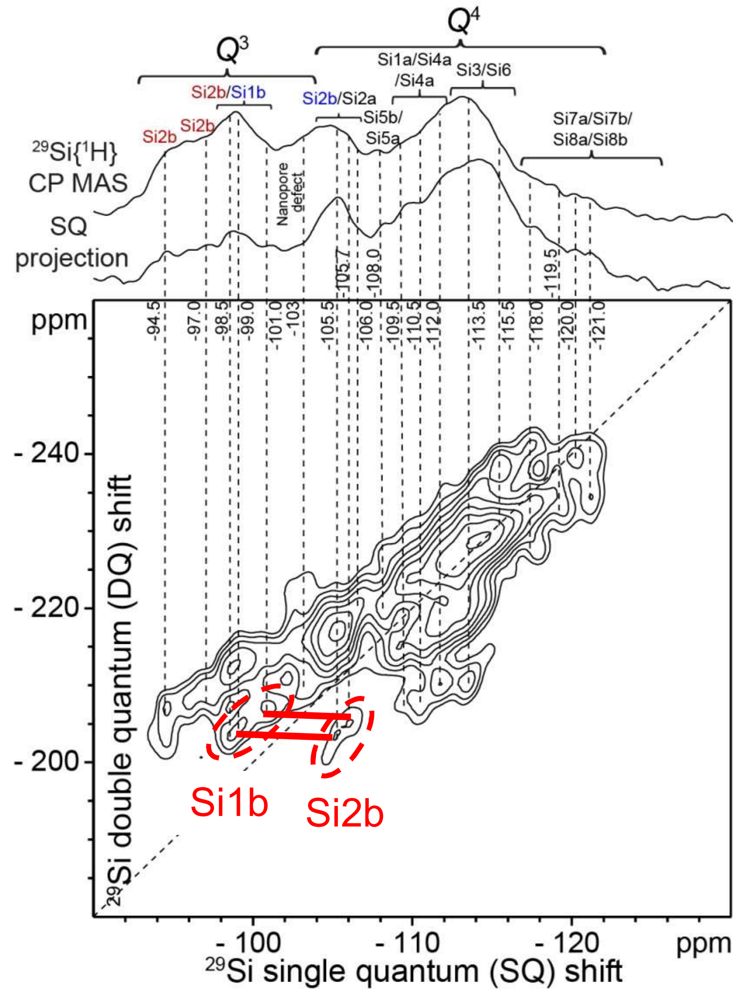




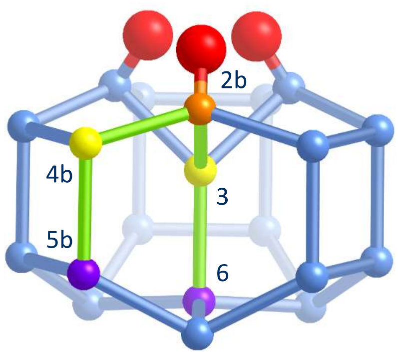
2D DNP-enhanced *J*-mediated $^{29}Si\{^{29}Si\}$ NMR



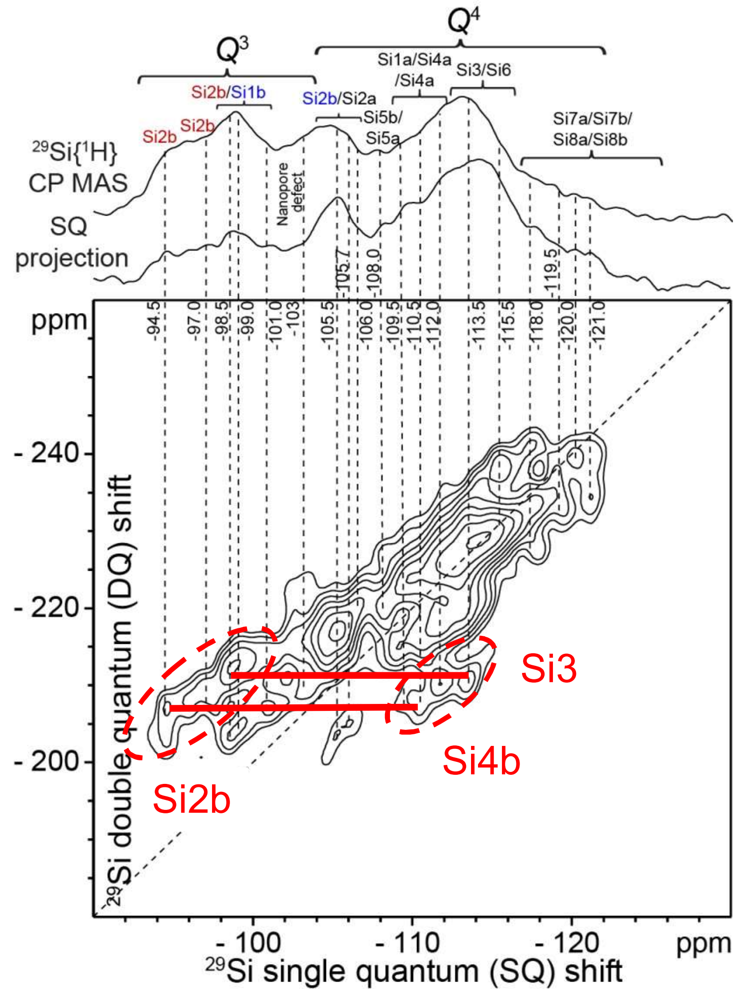
Model 1



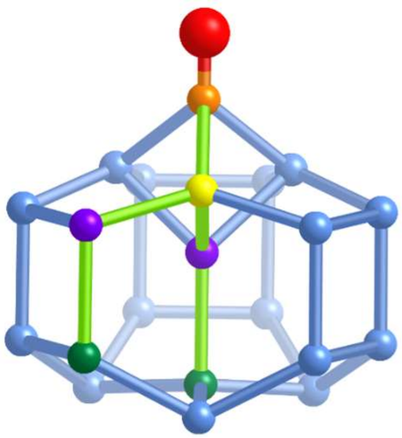
2D DNP-enhanced J-mediated $^{29}Si\{^{29}Si\}$ NMR



Model 2

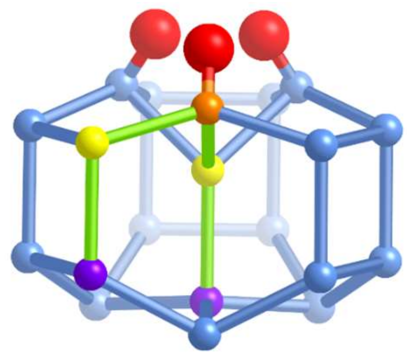


Interlayer region



Model 1

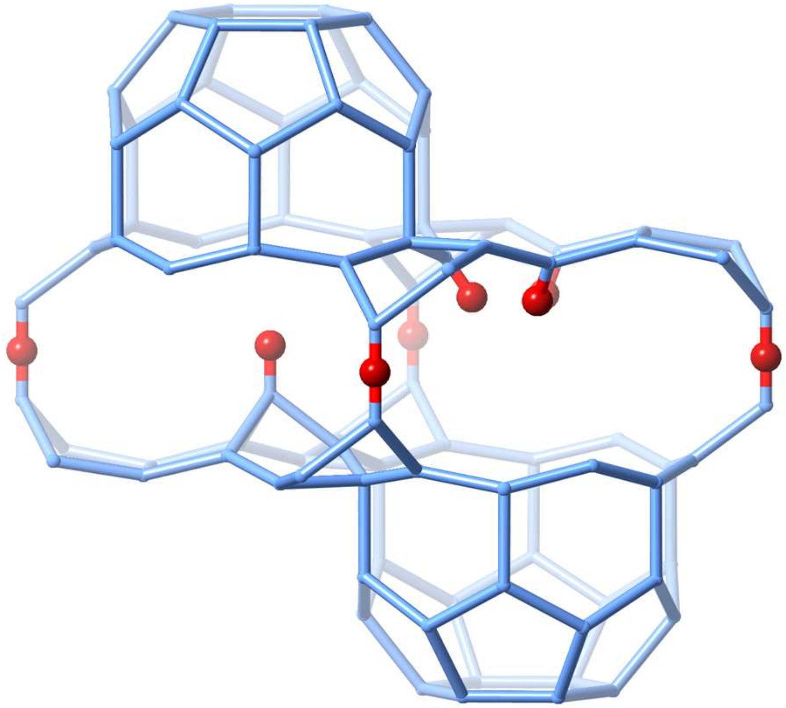
50%



Model 2

50%

Structure of calcined SSZ-70

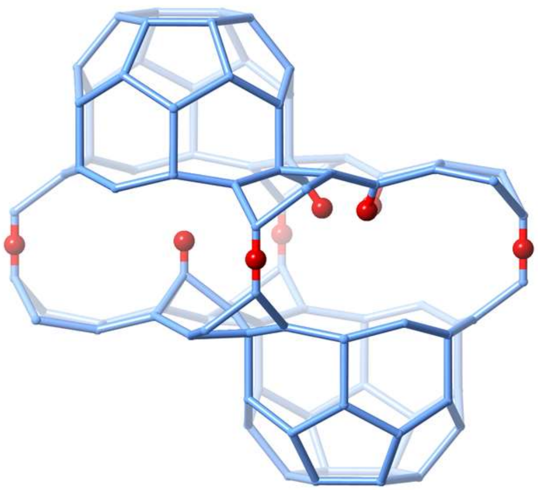


Summary SSZ-70

- Structure of SSZ-70 determined by combining methods
  - HRTEM → Short-range order
  - XRPD → Long-range order
  - 2D NMR → Nanostructure

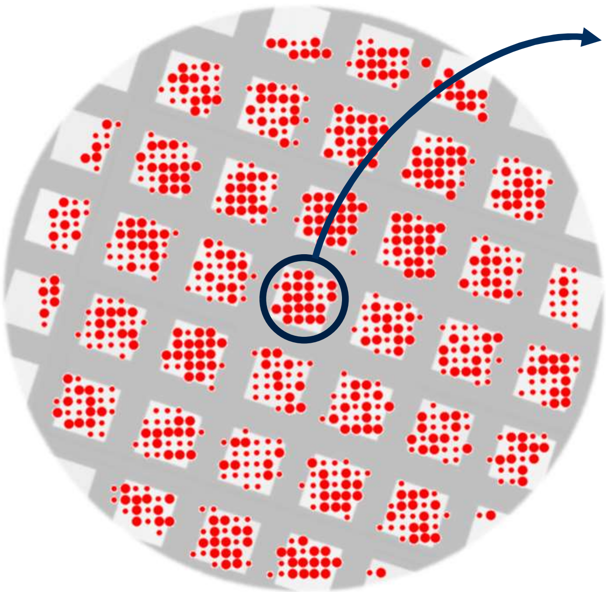
- New stacking arrangement of **MWW**-layers

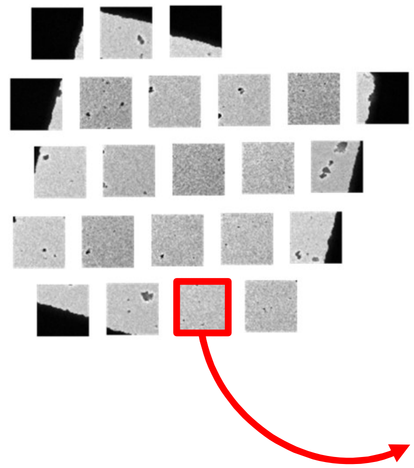
- Mixed silanol sites at the nanoscale can help explain enhanced catalytic behaviour of SSZ-70

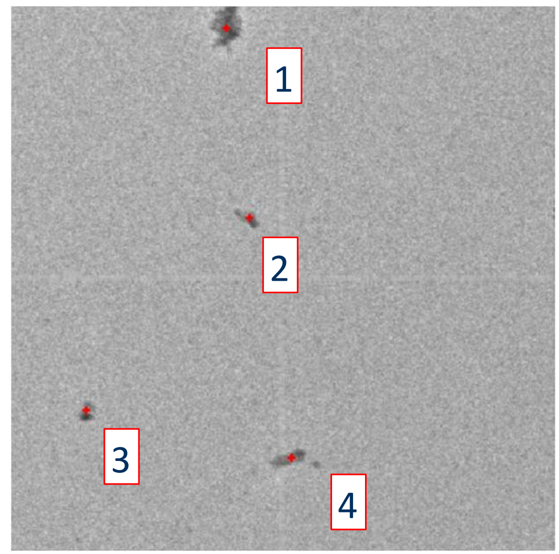


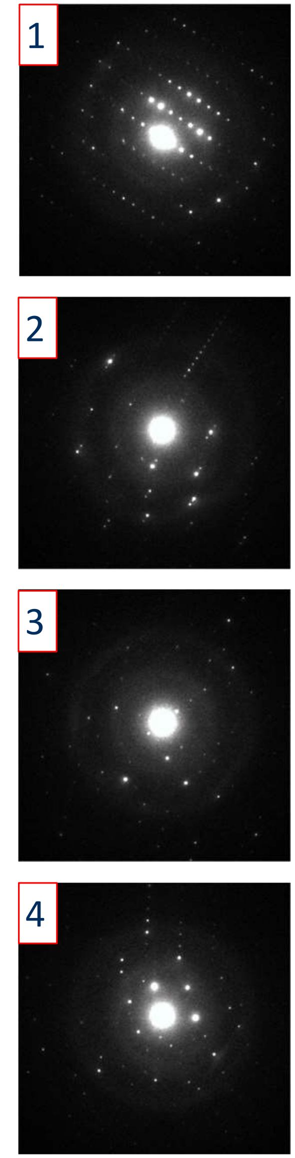
Serial electron diffraction

Serial electron diffraction







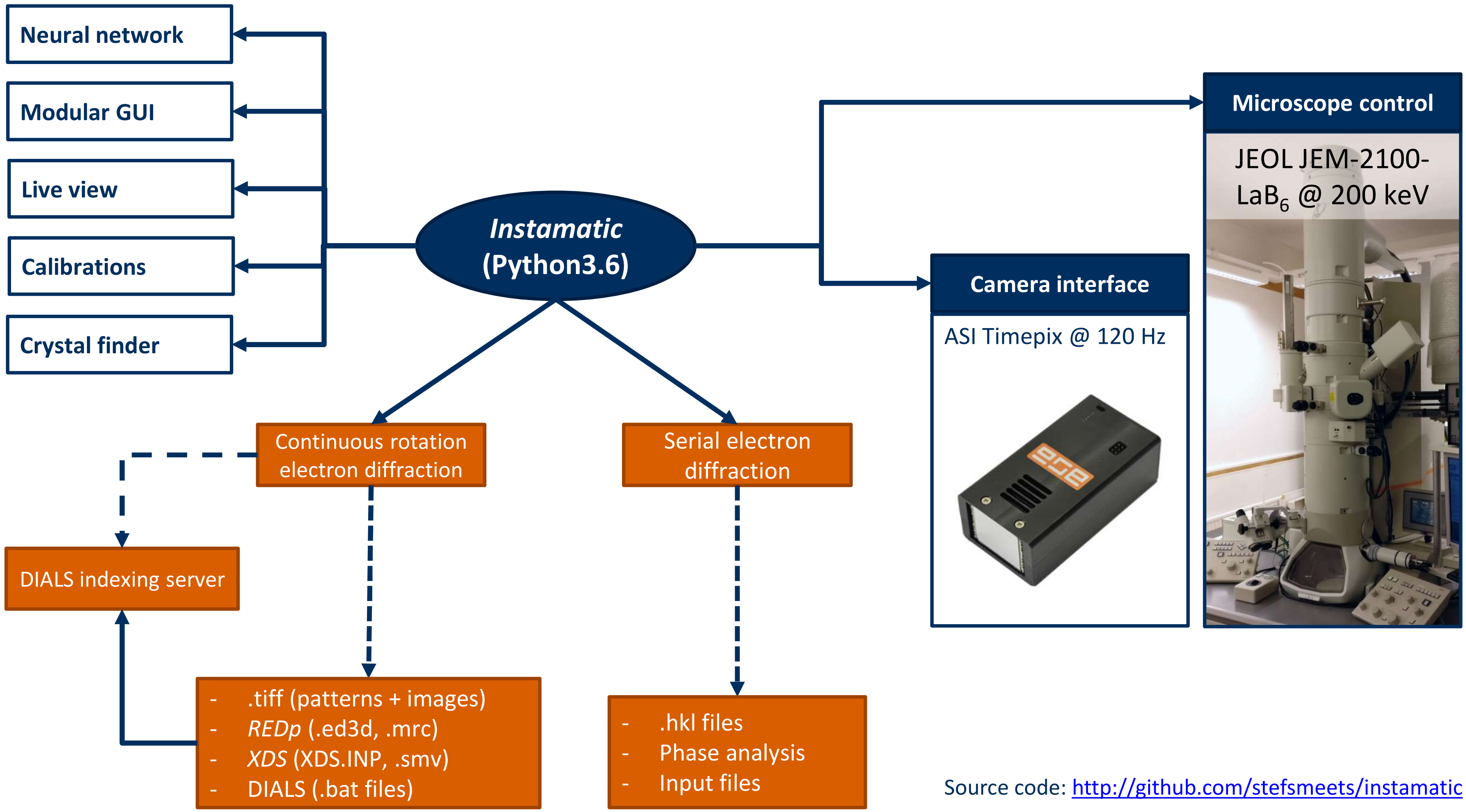


Randomly oriented crystals

1 crystal = 1 diffraction pattern

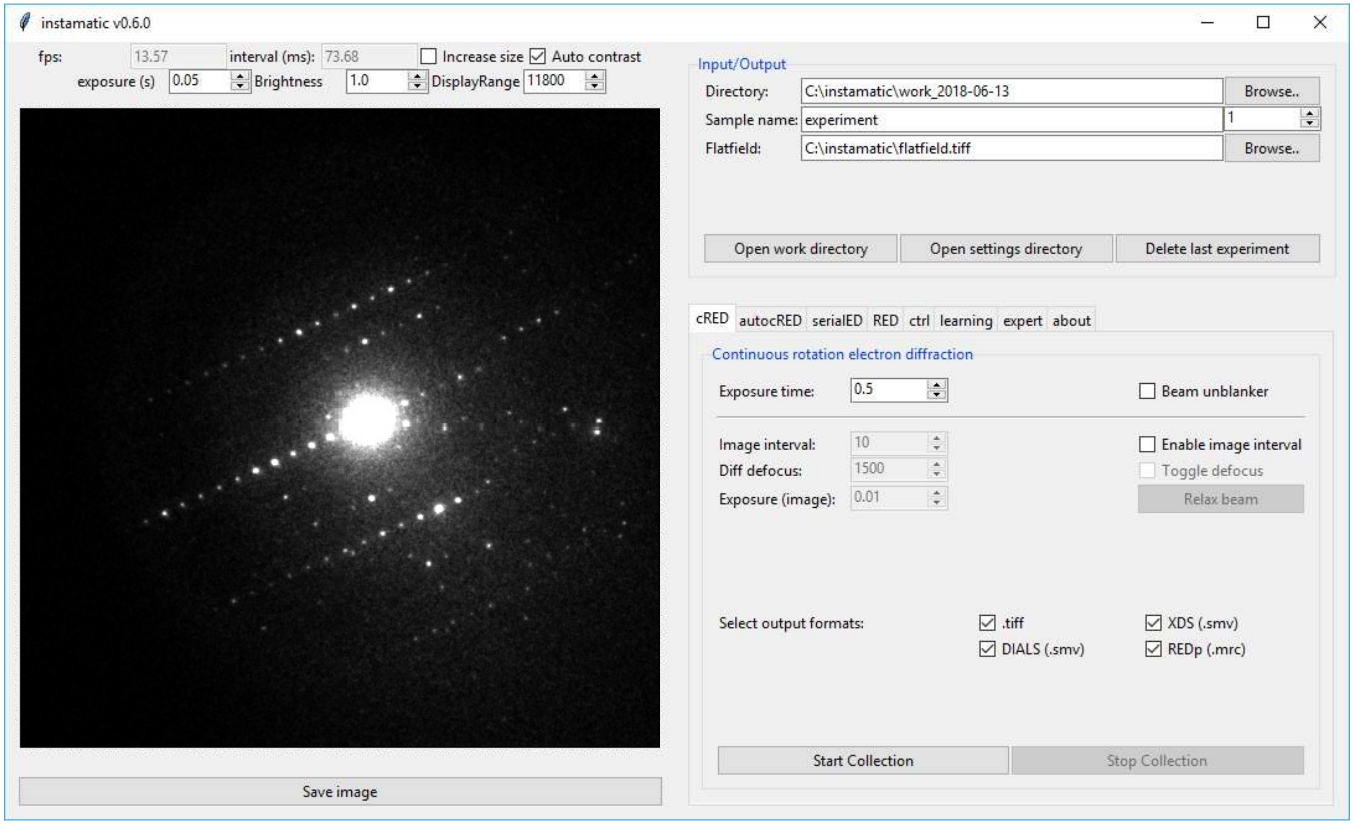
Combine data from many crystals

Collect data ~3000 crystals/hour

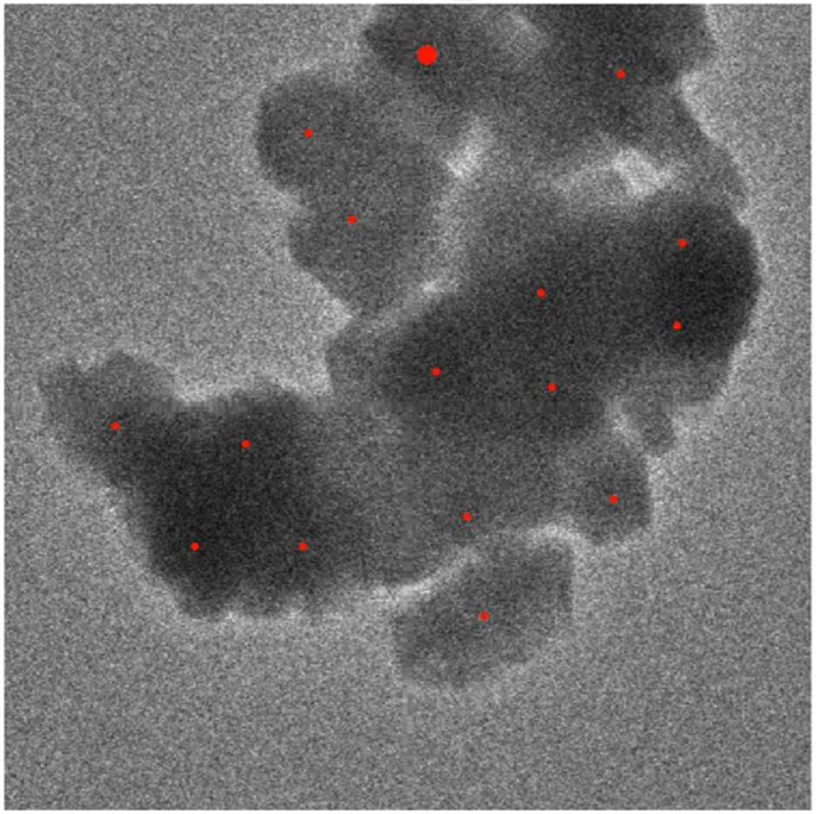


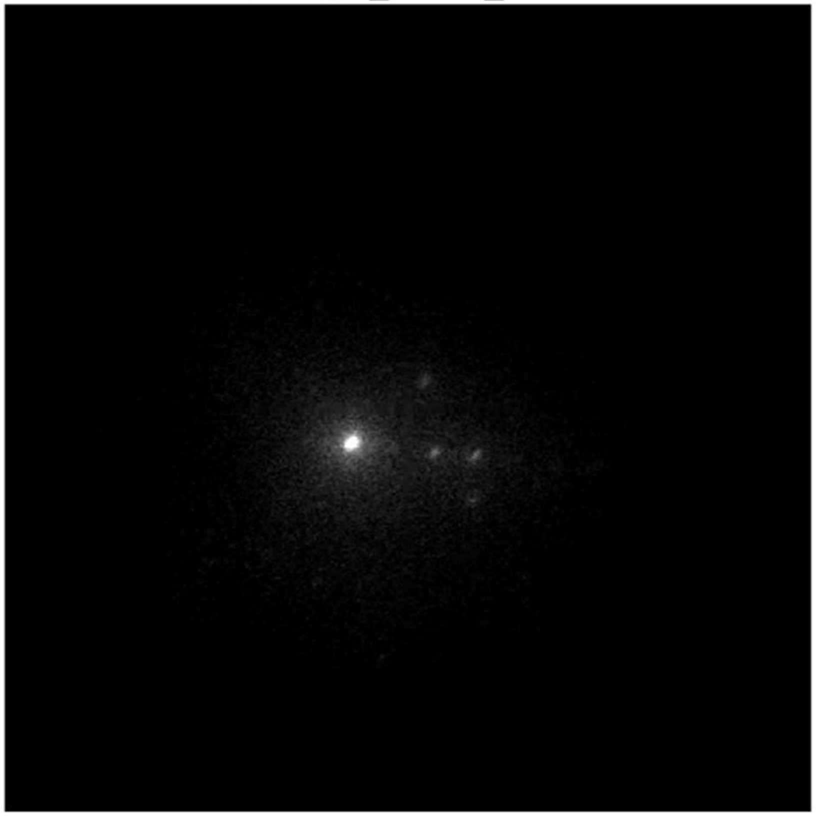
Source code: http://github.com/stefsmeets/instamatic

GUI for data collection

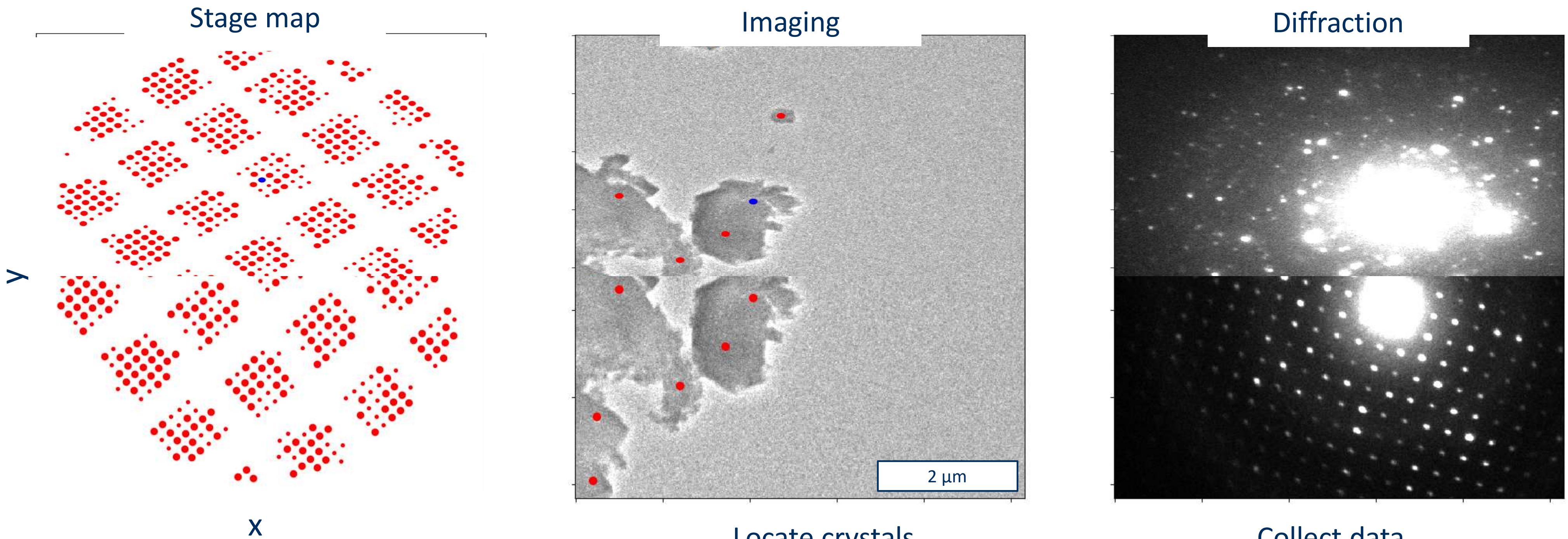


Data collection (Zeolite Y)





Data collection (zeolite A)



200 x 200 µm
484 images
35 minutes

Locate crystals

Probe size ~500 nm

Collect data

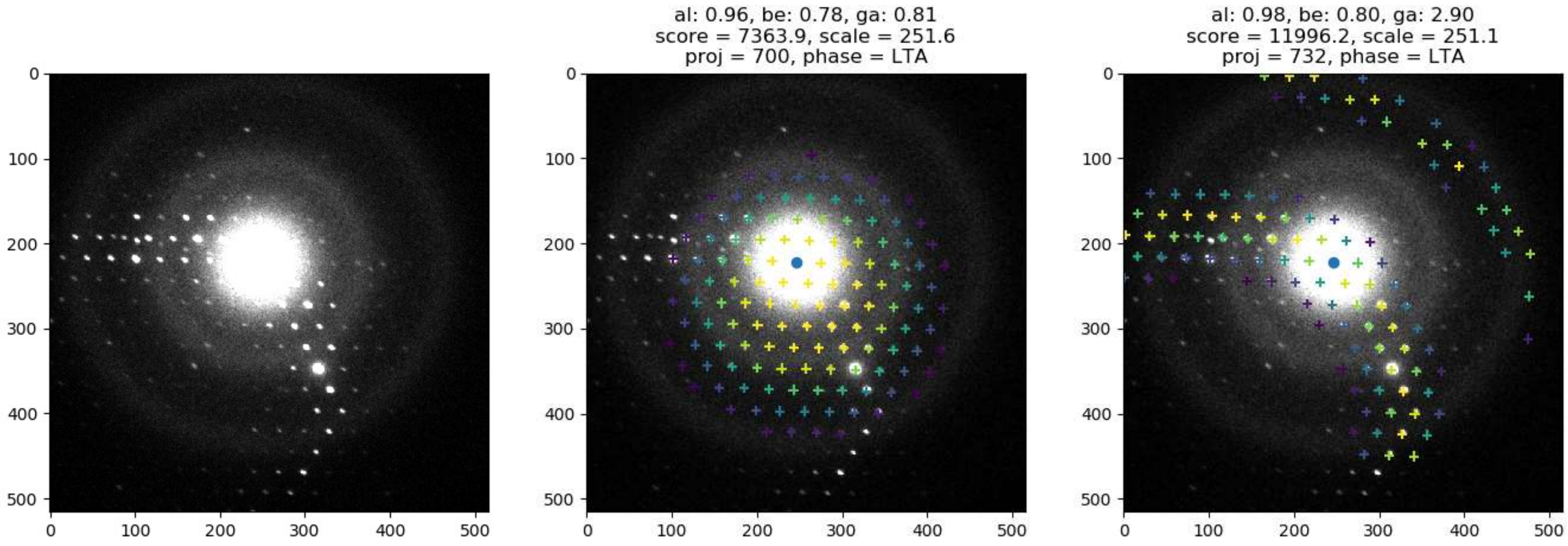
Total: 1107 patterns

Serial electron diffraction

→
- Structure determination?
- Phase analysis?
- Screening?

Structure determination: orientation finding

- Forward projection model using known lattice parameters
- Generate pattern library of all possible orientations (~1.5M in $P1$)
- Match best orientation and index data



Source code:
www.github.com/stefsmeets/problematic

Based on: Rius *et al.*, IUCrJ (2015), 2:452

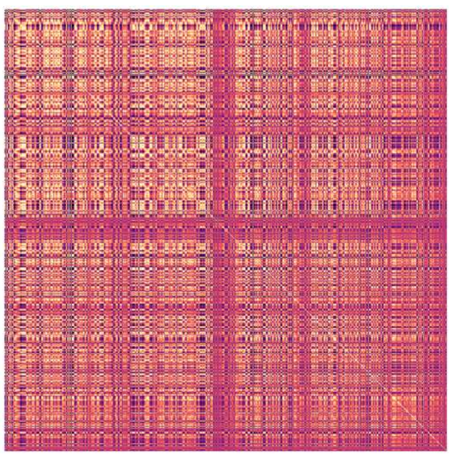
Structure determination: Data Merging

Challenges

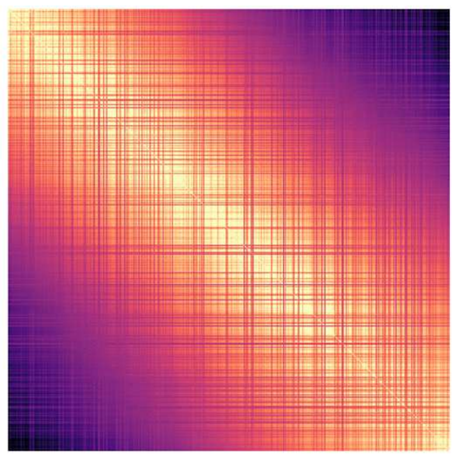
- Scaling
- Dynamical effects
- Reflection partiality

SerialMerge – rank-based merging

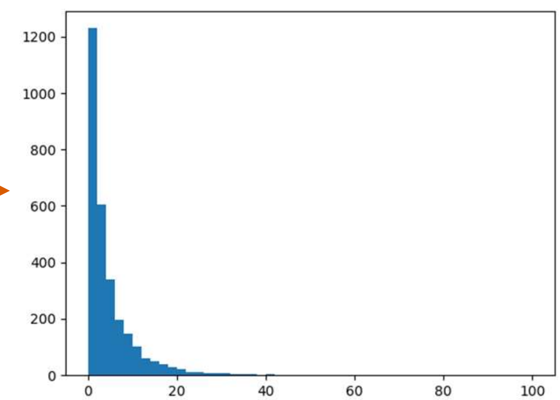
- Avoid scaling
- Avoid modelling intensities
- Robust with low quality data



Retrieve ranking

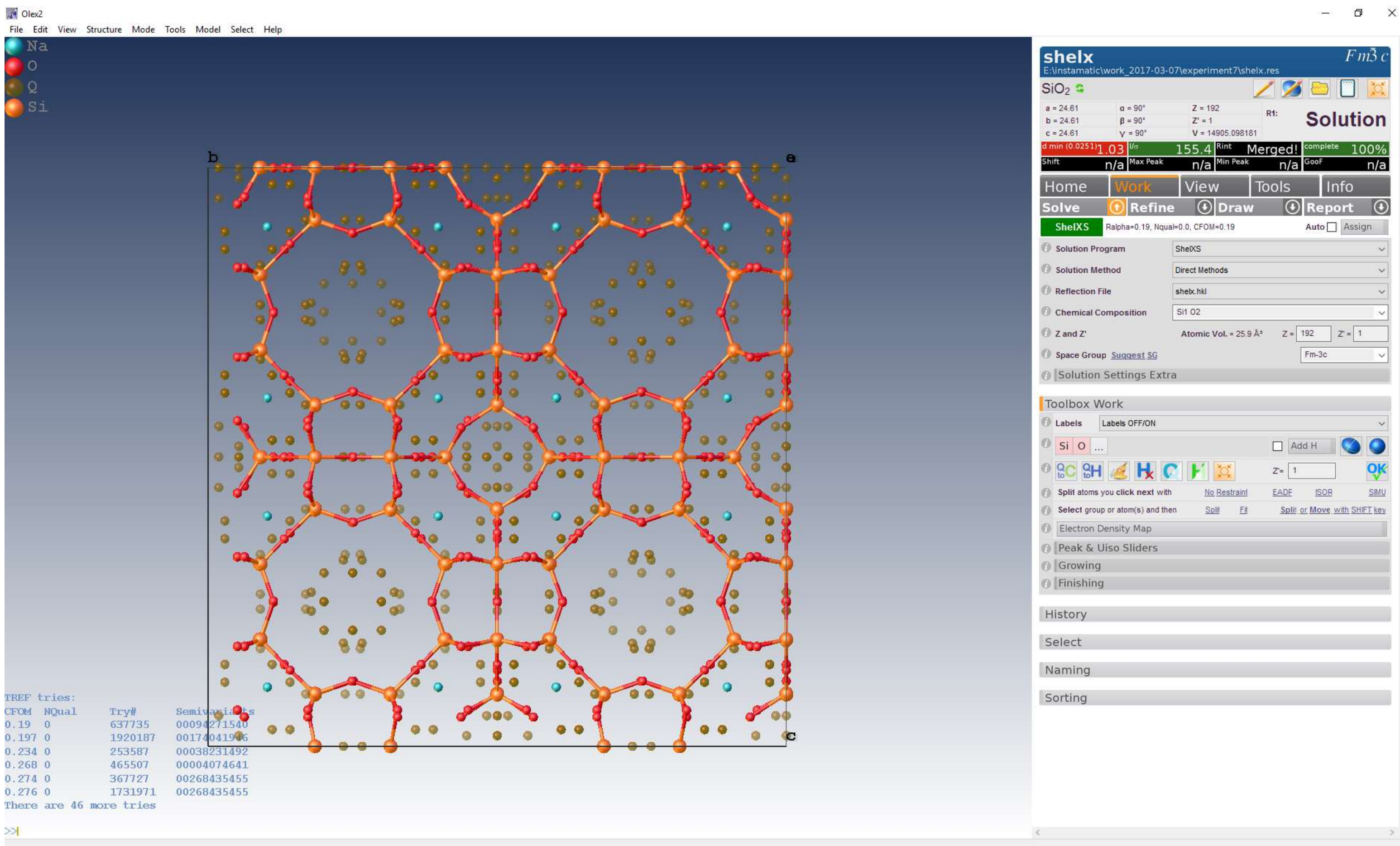


Apply $|F|$ histogram



S. Smeets & W. Wan, *J. Appl. Cryst.* (2017). **50**, 885-892
www.github.com/stefsmeets/serialmerge

Structure determination



Zeolite A

$Fm\bar{3}c$

$a = 24.61$ Å

$Si_{96}Al_{96}O_{384}$

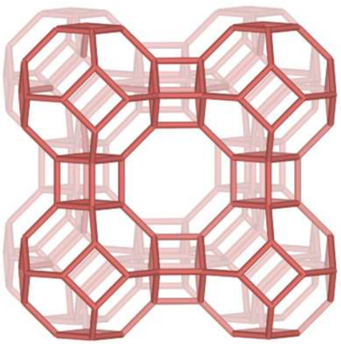
$Z = 192$

200 frames

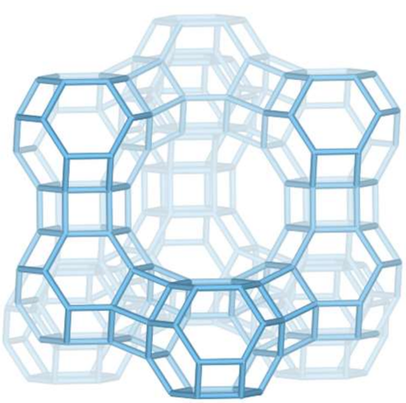
Reflections

Total:	19804
Unique:	227
d_{min}:	1.03 Å
Compl.:	100%

Structures solved

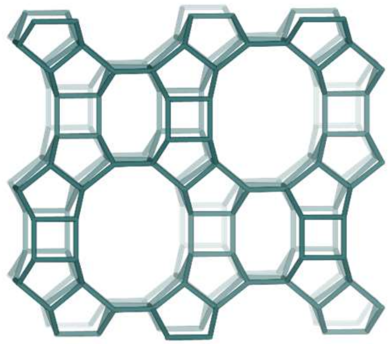


Zeolite A
$Fm\bar{3}c$
$a = 24.61$ Å
$Si_{96}Al_{96}O_{384}$
$Z = 192$

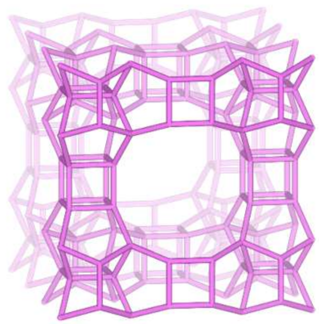


Zeolite Y
$Fd\bar{3}m$
$a = 24.74$ Å
$Si_{192}O_{384}$
$Z = 192$

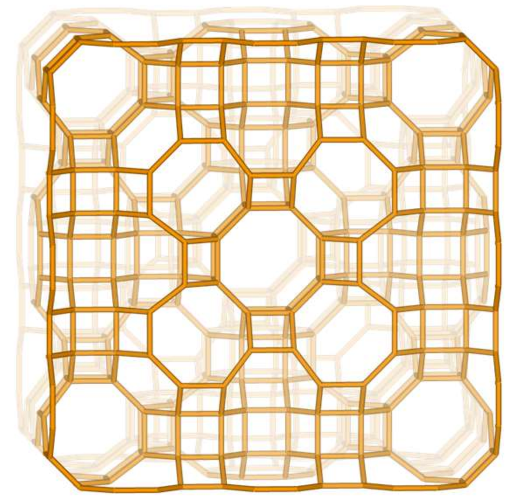
Direct methods
ShelXS



Mordenite
$Cmcm$
$a = 18.11$ Å
$b = 20.53$ Å
$c = 7.53$ Å
$Si_{40}Al_8O_{96}$
$Z = 16$



Ge-BEC
$P4_2/mmc$
$a = 12.82$ Å
$c = 13.35$ Å
$Si/Ge_{32}O_{64}$
$Z = 16$



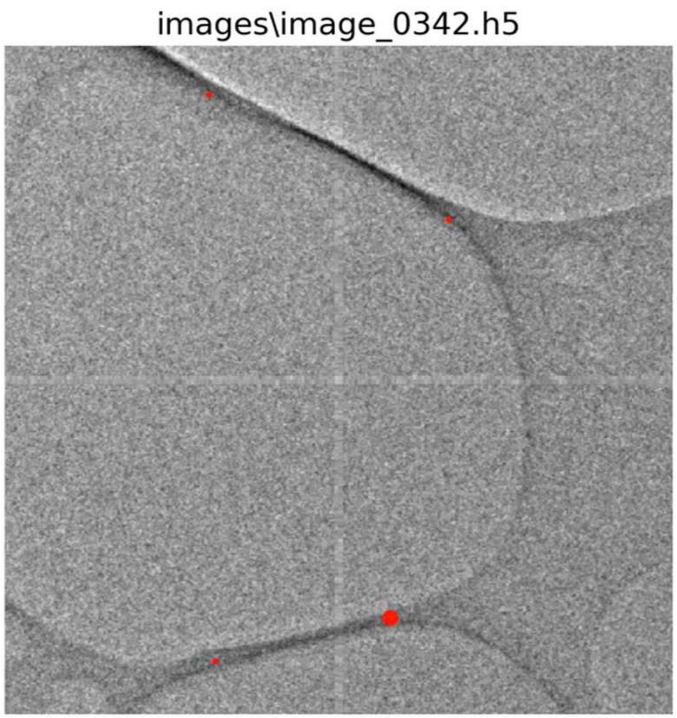
Paulingite
$Im\bar{3}m$
$a = 35.08$ Å
$Si_{672}O_{1344}$
$Z = 96$

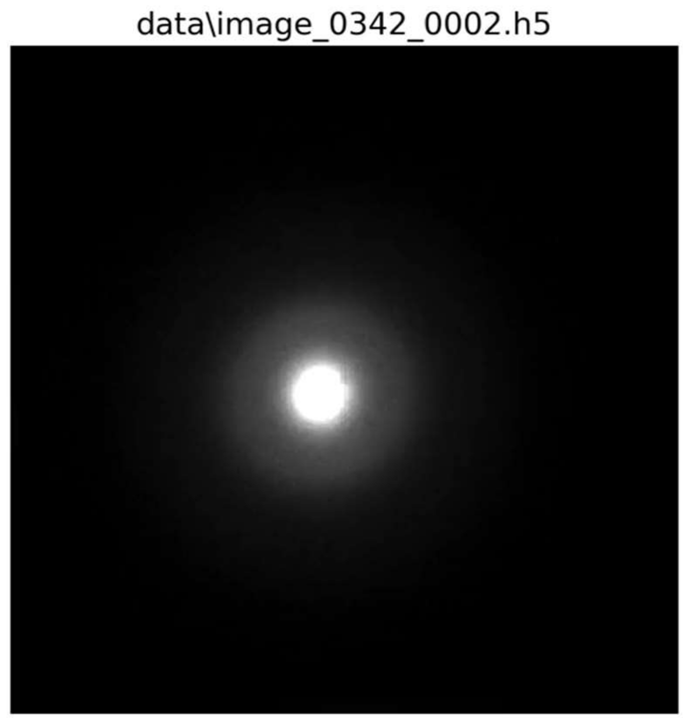
Dual-space methods
FOCUS

Serial electron diffraction

- Structure determination?
- Phase analysis?
- Screening?

Phase analysis: Co-CAU-36

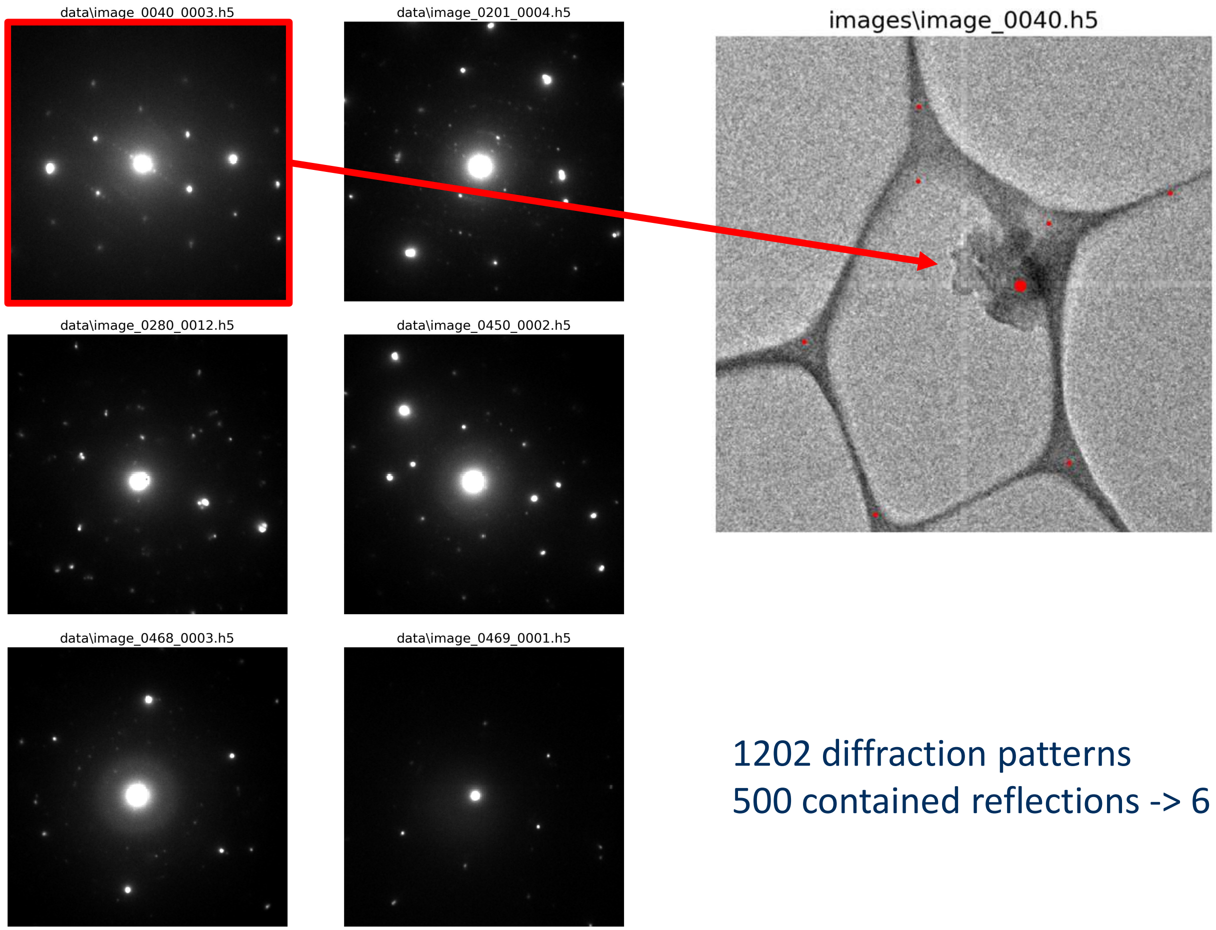


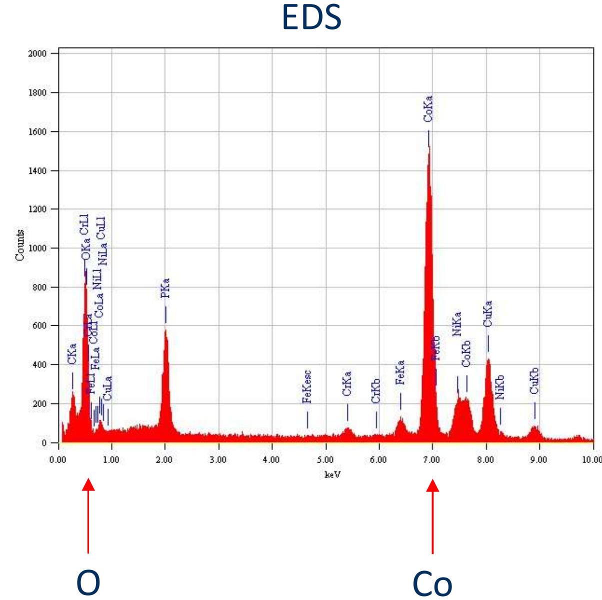


Scan 200 x 200 µm in 30 minutes
1202 diffraction patterns

Sample from Bin Wang & Ken Inge (Stockholm University)

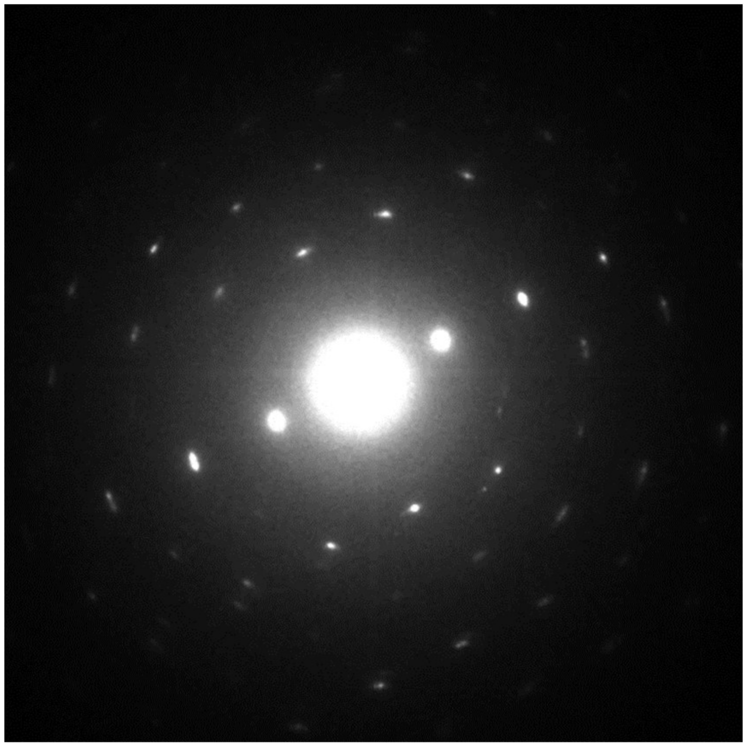
Phase analysis: Co-CAU-36

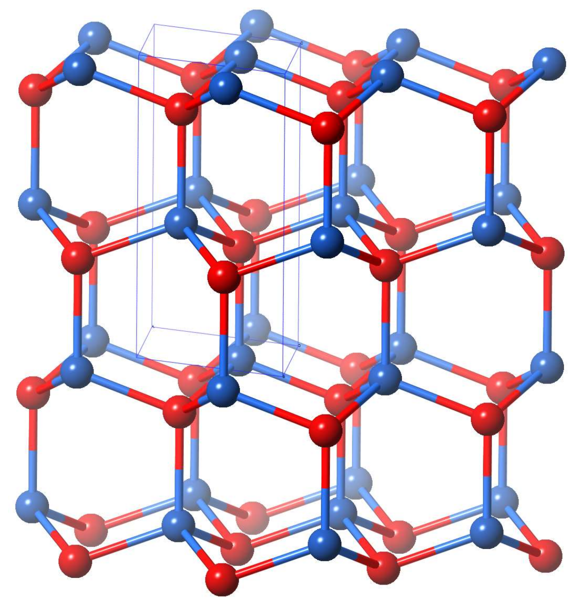




1202 diffraction patterns
500 contained reflections -> 6 impurity crystals

Phase analysis: Co-CAU-36



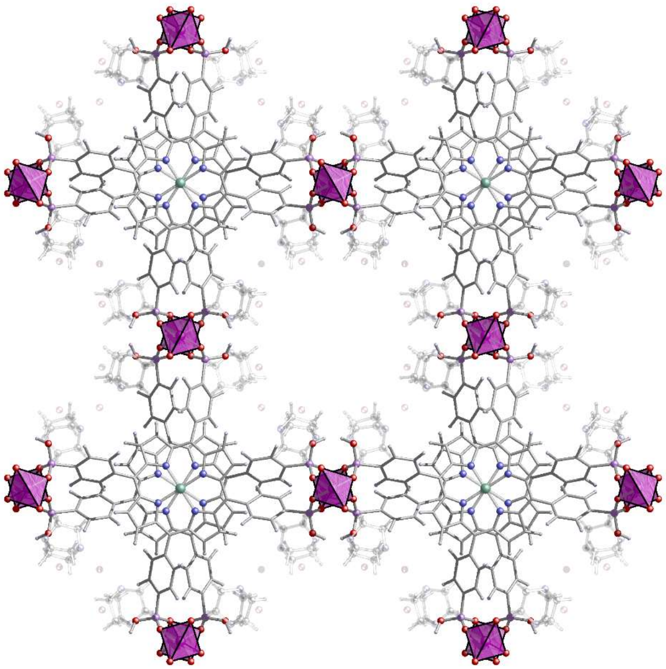


34.45 to -13.79°
Oscillation angle: 0.23°
1.5 min data collection

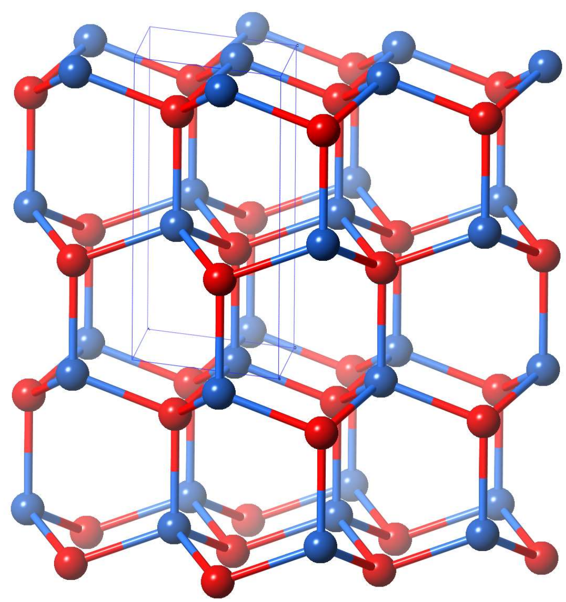
XDS →

P6_3*mc*
a = 3.10 Å, *b* = 5.45 Å
Wurtzite structure (CoO)

‘Quantitative’ phase analysis



Co-CAU-36: ~99%
494 patterns

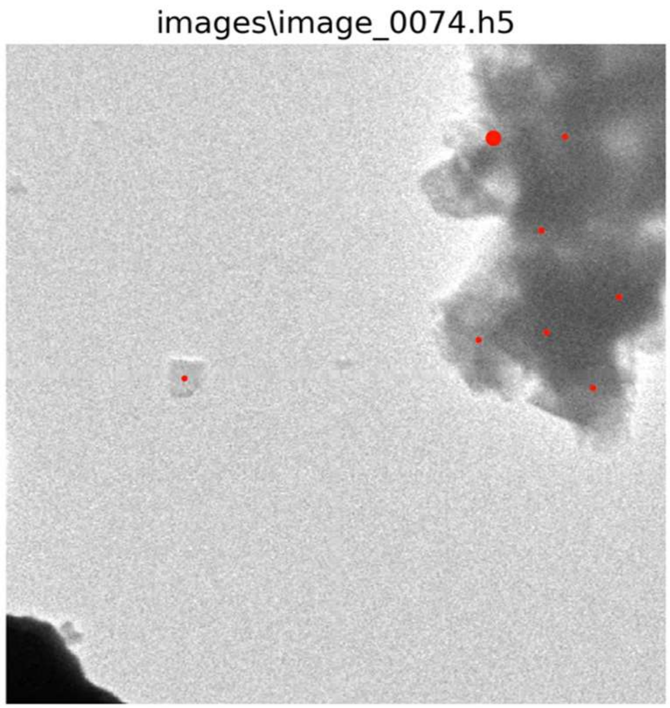


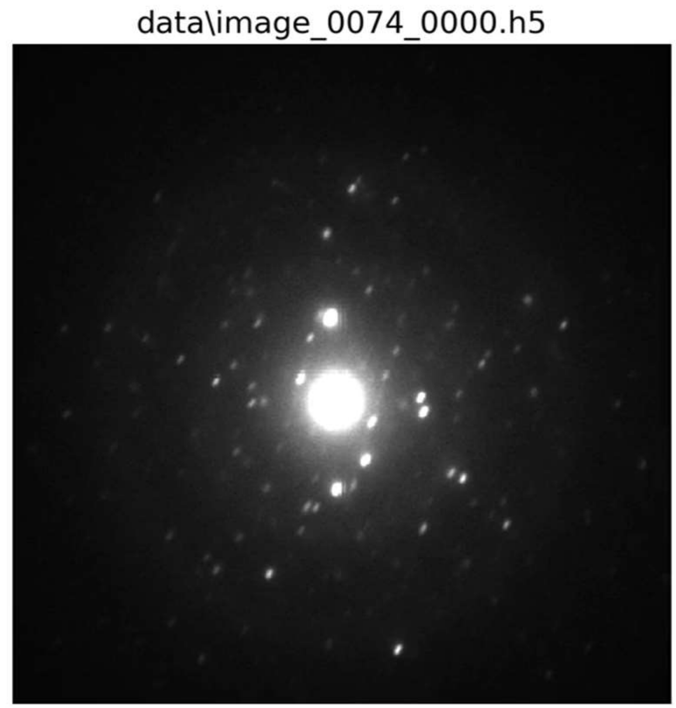
CoO (wurtzite): ~1%
6 patterns

Serial electron diffraction

- Structure determination?
- Phase analysis?
- → Screening?

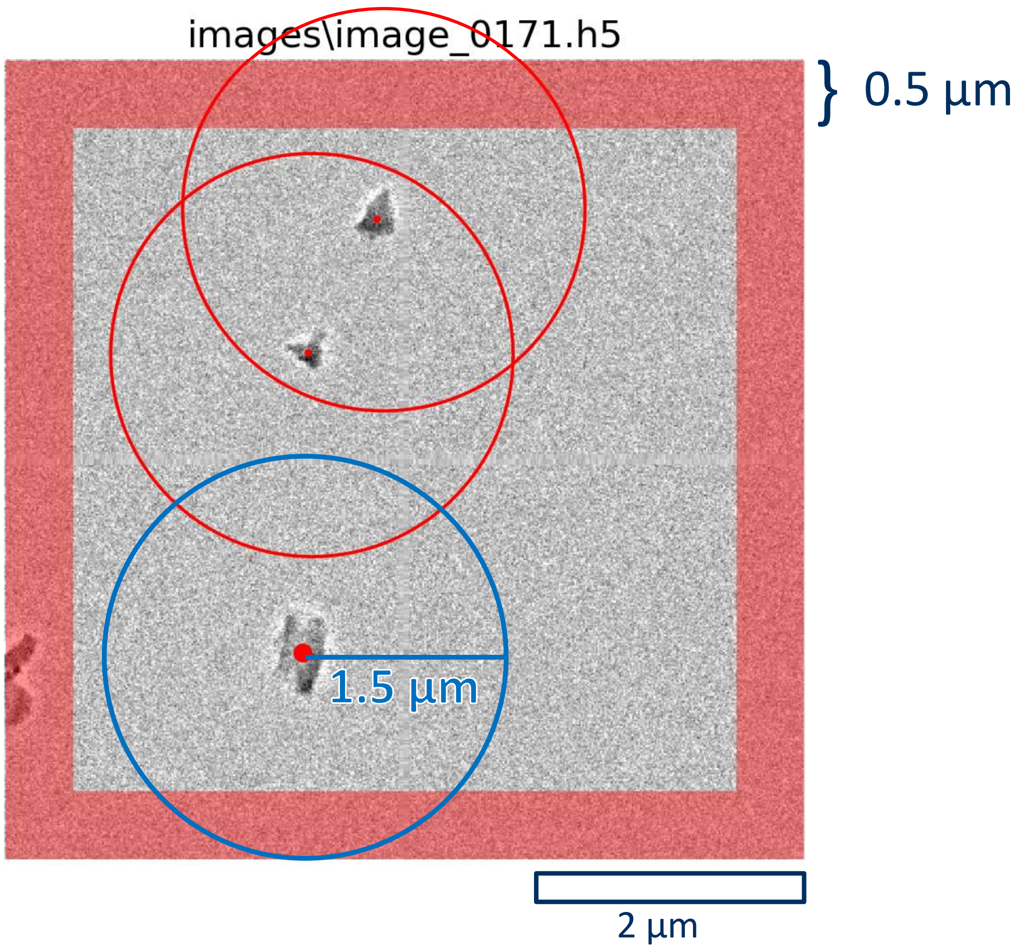
Screening: Mordenite





Scan 200 x 200 µm in 24 minutes
836 diffraction patterns (2090 / hour)

Screening: Crystal selection



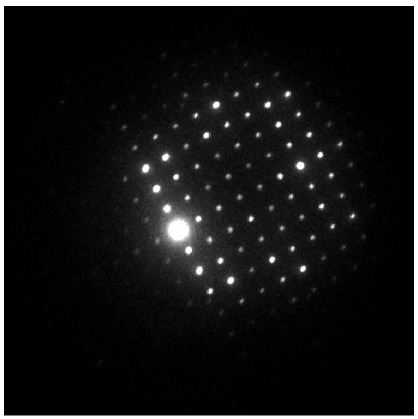
Crystal selection

1. Find isolated crystals
   - Must be 0.5 µm away from edge
   - No crystals in 1.5 µm radius

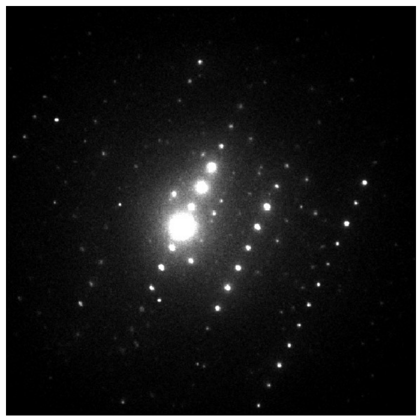
2. Select most suitable crystals
   - Machine learning (CNN)

Screening: Machine learning

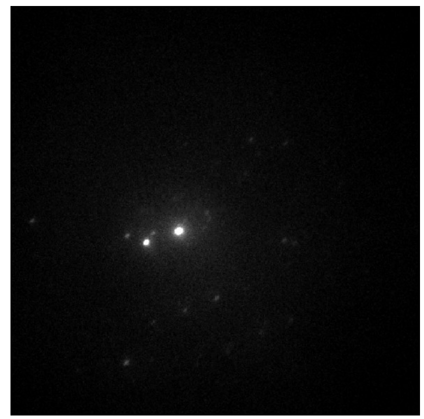
- A deep convoluted neural network trained on ~78.000 diffraction patterns predicts which crystals are suitable for collecting CRED data



Prediction: 1.0



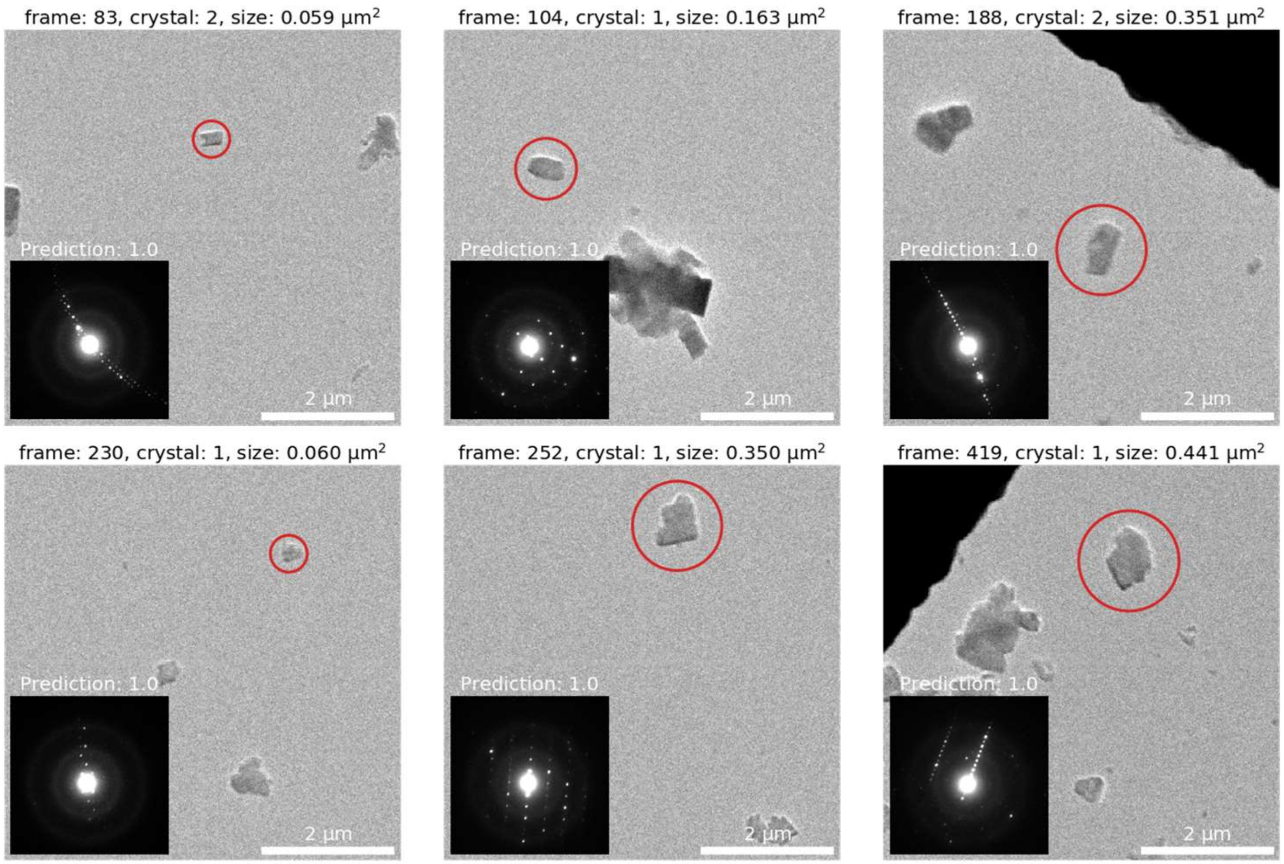
Prediction: 1.0



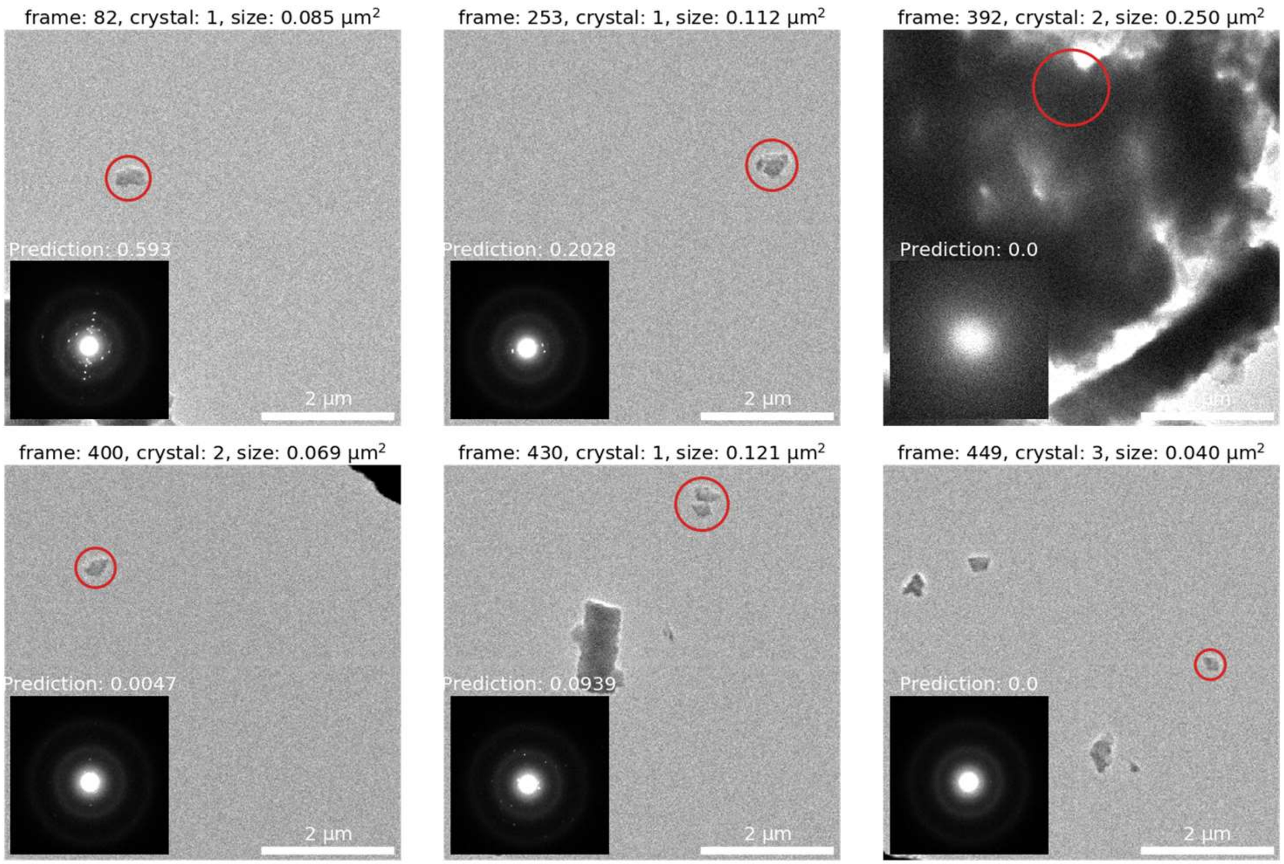
Prediction: 0.26

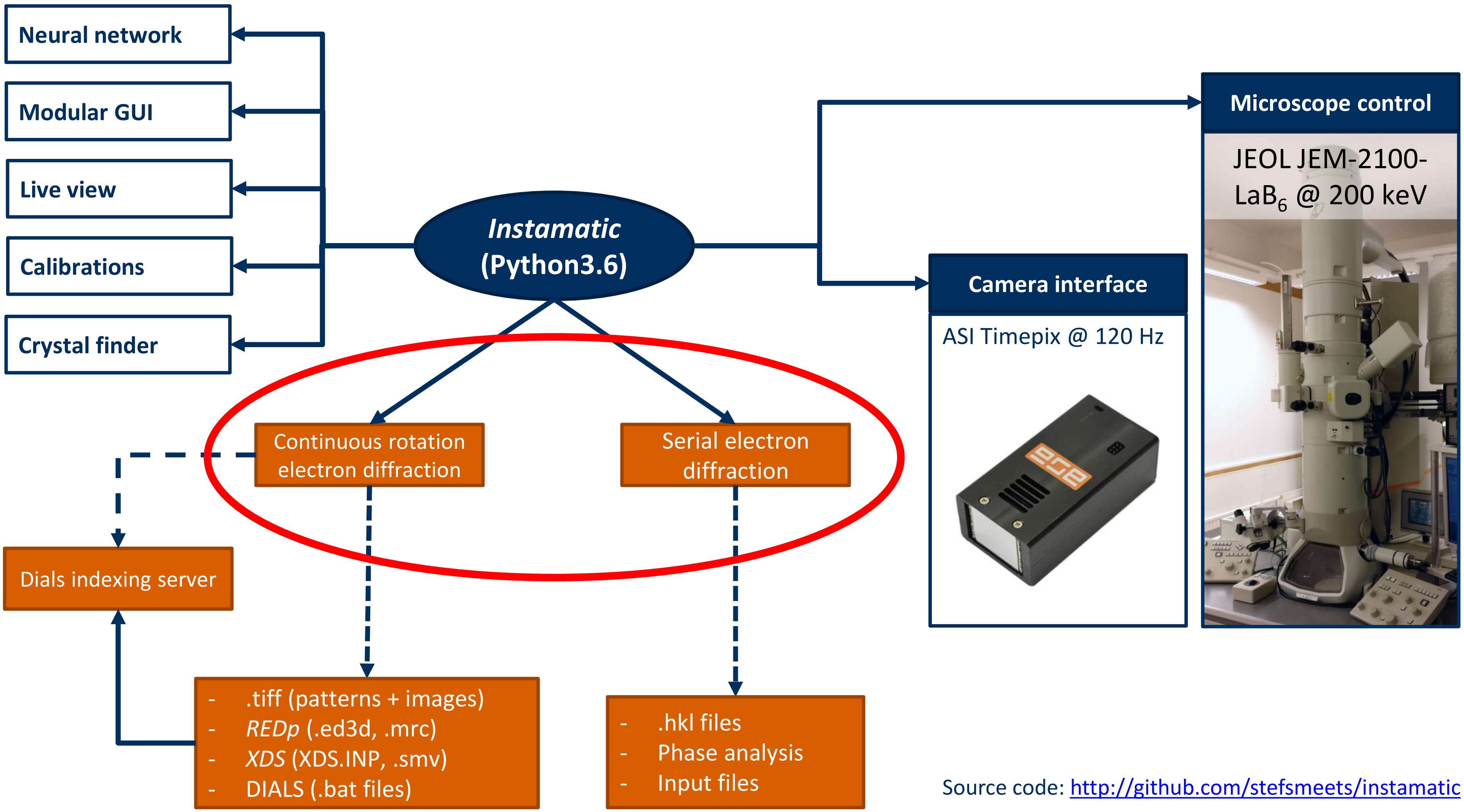
Prediction: 0.25

Screening: 6 of the ‘best’ crystals (53)



Screening: 6 of the ‘worst’ crystals (53)

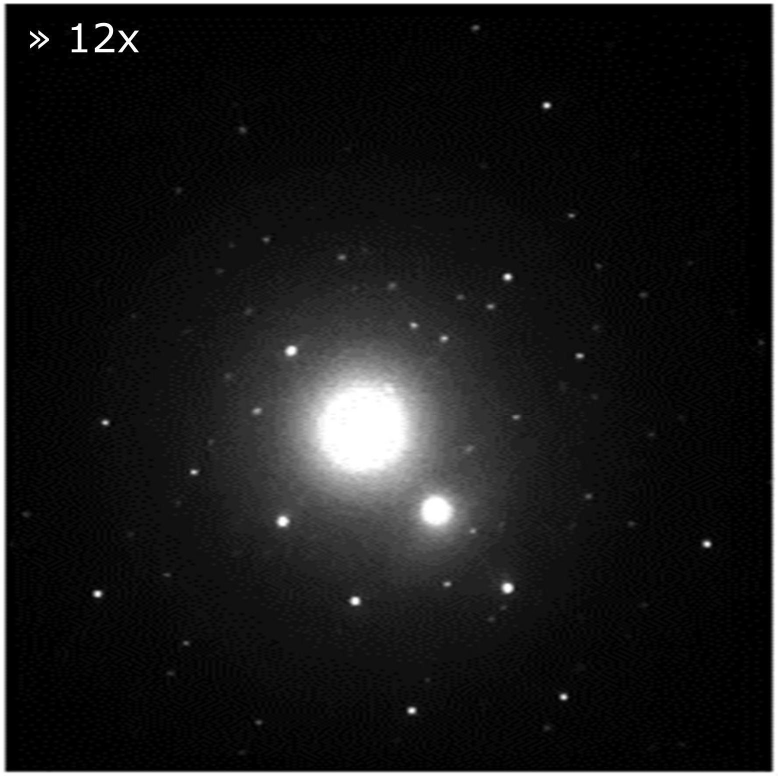


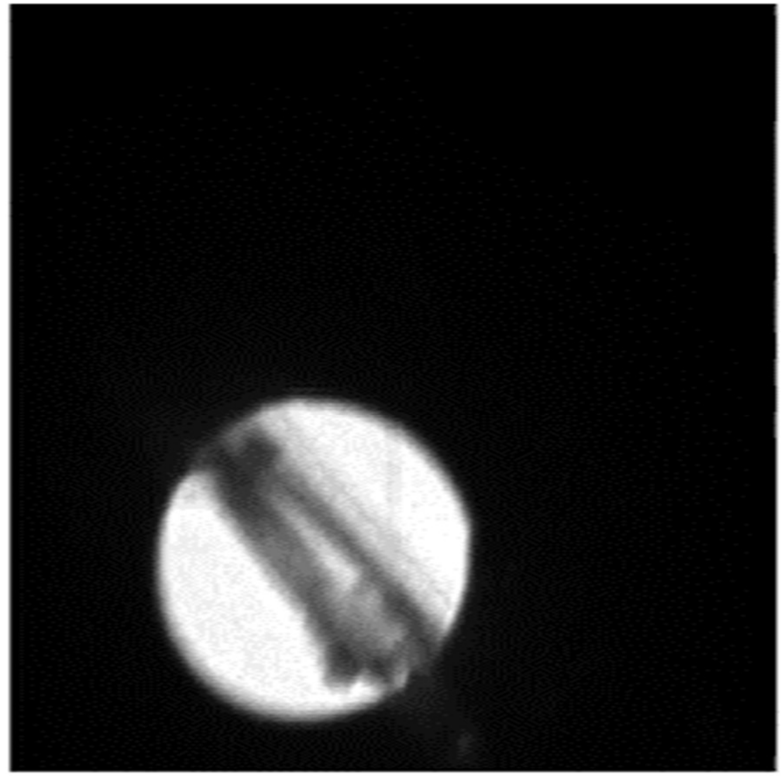


Source code: http://github.com/stefsmeets/instamatic

Automated data collection

Rotation: -44.0 to 47.4° @ 0.76°/s (91.4°)
Exposure: 0.5 s, oscillation angle: 0.39°





Data collected by Bin Wang (Stockholm University)

Conclusions

- Electrons are very well suited for structure determination
  - Reliable crystal structures can be obtained
- PXRD data are valuable for
  - Structure validation against bulk material
  - Structure completion (*e.g.* cations/templates/adsorbants in zeolites)
- Combination of methods is essential to find all the details
- SerialED data can be collected routinely & automatically
  - Structure determination
  - Phase analysis
  - Screening
- Future: Combined SerialED and CRED for automated crystal picking and data collection